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LXVIII. *The Electrical Behaviour of Radioactive Colloidal Particles of the Order of* 10^{-5} *cm. as observed separately in a Gas.* By FELIX EHRENHAFT, *Dr.Phil., Acting Professor of Physics and Head of Physics Institute III. of the University of Vienna* *.

§ 1. UNTIL a few years ago all the observational data which we possessed were sufficiently explained by the Rutherford hypothesis—that the α-particles of radioactive substances all had identical charges and properties. Lately, again, Henderson †, experimenting with α-particles which had passed through matter, deduced that they can carry double or single charges or be uncharged. I am interested, nevertheless, in those experiments of the Rutherford school where Kapitza ‡ has succeeded in photographing the tracks of α-particles under a strong magnetic field in a Wilson chamber. It was found that these tracks were of various kinds, having each its own curvature The writer had already pointed out, some years § ago, that all deductions concerning α-particles had to do with average values, and that we could not really speak of having determined the actual *individual* charges. This idea seems to have received definite support from Kapitza's experiments, for the experimenter himself treats the separate α-particle charges as a function of the distance travelled, and the reader of the

* Communicated by the Author.

† Proc. Roy. Soc. cii. p. 496 (1923).

‡ Proc. Camb. Soc. xxi. p. 511 (1923).

§ *Wiener Akad. Ber.* cxxiii. (ii. *a*) p. 61 (1914); *Ann. d. Phys.* xliv. p. 664 (1914); *cf.* also, *Wiener Akad. Ber.* cxix. (ii. *a*) p. 816 (1910).

article can see that the charge of one single α-particle, for example, varies from 2×10^{-10} to 7×10^{-10} e.s.u.

This state of affairs induces me to draw attention to investigations which I have been carrying on for more than fifteen years and which may be of interest for their application, set out in detail below, to radioactivity and as bearing directly on these experiments of the Rutherford school.

§ 2. The charge on the electron enters as a fundamental physical constant into many theories of modern physics as well as into the science of radioactivity. As early as 1910 the writer had strongly emphasized the idea *, that it was only by averaging the observations on groups of particles, or other averaging processes, that one could obtain the elementary indivisible quantum charge on the electron, as demanded by the fundamental hypothesis of the electron theory. The writer had himself observed the motions of small spherical particles of silver, of the order of 10^{-5} cm., in a gas, and, by averaging, had deduced † a charge for these particles of the order of the so-called elementary quantum. It was clear, however, that such a procedure, where average values are depended upon, is incomplete. For this reason, even before the publication of these results, the writer had given a method ‡ (*Anzeiger d. Wiener Akad. d. Wiss.* no. vii.

* Vide *loc. cit.*

† *Wiener Akad. Ber.* cxviii. (ii. *a*) p. 321 (1909).

‡ Since Prof. Millikan has opened up, in several English publications, the question of priority in the method of determining electric charge on individual particles, and since, by reason of the war, I could only reply in German ones (*Ann. d. Phys.* lvi. p. 58, 1918), I should like to be allowed to make the following remarks:—

Prof. Millikan has changed his standpoint on the priority question, for, at first, he wrote in the Phys. Rev. xxxii. p. 392, April 1911: "The only other investigations which appear to yield results which are in any way adverse to the conclusions herein contained are reported in very recent papers of Ehrenhaft and Przibram, both of which have appeared since this work was first presented to the Physical Society on April 23, 1910." His contention was thus, all this time, limited to independence in discovery of the method. On the other hand, he wrote later on, in the Phys. Rev. viii. (n. s.) p. 596, Dec. 1916, as follows: "Ehrenhaft, in a paper read at the Naturforschersammlung zu Königsberg in Sept., 1910, made a very clear statement of this defect in his own attempted determination of *e*, and asserted that it inhered also in the work of all other observers. *As a matter of fact, however, I had the good fortune to find a way of removing this limitation entirely more than a year earlier, viz., in the spring and summer of 1909.*" He is here already claiming priority and in fact modifying the standpoint he had taken up to this time, as is shown by his article in Phil. Mag. xix. p. 209, Feb. 1910, concerning which we shall have something to say below. In 1917 he goes so far, indeed, as to write in Phil. Mag. xxxiv. p. 1, July 1917: "For, first, Professor Ehrenhaft and his pupils began publishing in 1914 a

March 4, 1909 ; no. x. April 21, 1910 ; no. xiii. May 12, 1910) enabling us to determine the charge on the smallest possible

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series of results which, though obtained by a modification of my method, were wholly irreconcilable with the results which I had found." That is, he now dates the beginning of my writing about five years too late, a presumption which cannot be entertained.

The actual state of affairs is, however, as follows: As early as the no. 7 issue, March 4, 1909, of the *Anzeiger der Wiener Akad. d. Wiss., i. e.* before the publication by any other writer on this point, I expressly pointed out that the measurement of the electric charge on *single particles* supplied a new method for the determination of the elementary electric quantum. Also in an exhaustive article of March 18, 1909, in *Sitzungsber. d. Wiener Akad.* cxviii. (ii. *a*) p. 321 and in the *Phys. Zt.* x. pp. 308–310, I established the fact that the method I had developed for measuring charges could be applied to individual particles and would enable us to calculate the charge of a single particle. Millikan, on the other hand, has not pointed out the *necessity* for measurements by the aid of single particles either in his preliminary communication of Dec. 1909 (Phys. Rev. xxix. p. 260) or in his more complete paper on cloud particles, Phil. Mag. xix. p. 208, Feb. 1910. Neither is this to be wondered at, for, as can be clearly seen from the last named article, he arrived only accidentally at the method of observations on single particles. (In this connexion, *cf.* lines 20 to 32, p. 2'6, of the article in question.) Accordingly he does not apply his readings to these particles separately—a point I have already made in the *Wiener Akad. Sitzungsb.* cxix. (ii. *a*) p. 825 (1910), and in the *Phys. Zt.* xi. p. 942 (1910)—but takes their mean. It was I who first recalculated Millikan's results for separate particles and could thus demonstrate, for example, that in a group to which he accorded 3 quanta he had averaged a water particle which by my calculation carried $15{\cdot}59\times10^{-10}$ e.s.u. Another water particle for which I calculated the separate charge of $15{\cdot}3\times10^{-10}$ e.s.u. was included in a group in which was given 4 quanta. It follows that my papers, which appeared in the Academy *Anzeiger* no. 7, March 4, 1909, no. 10, April 21, 1910, and no. 13, May 12, 1910; in the exhaustive article in the *Sitzungsber. d. Wiener Akad. d. Wiss.* May 12, 1910, and also the paper read at the Science Meeting at Königsberg (*Phys. Zt.* xi. pp. 940–949, 1910), are the first ones dealing with the charge on individual particles which discuss the question of the existence or non-existence of an electron. They are also the first in which observations were taken and calculations made on separate particles. On the other hand, Millikan's first papers in which he recorded and calculated from separate particles appeared first in Dec. 1910 in the *Phys. Zt.*, the first in English being in the Phys. Rev. of 1911. He, therefore, did not abandon the Wilson cloud method to adopt the method of observation and calculation with separate oil drops until Dec. 1910 in the *Phys. Zt.*

It is clear from this that the point of view that the existence of an elementary quantum was to be proved by measurements on individual particles was brought forward and carried out in the first place by the writer, whereas Prof. Millikan had up till then employed only charge averages, and this is of course quite easy to understand, for he had never had any doubt concerning the existence of an elementary quantum of electricity.

particle in a gas. This method was next treated exhaustively in several papers *, and again the point was discussed at large at the Science Meeting in Königsberg †. The fundamental idea in all this was that we can *most probably expect to find the smallest electric charge on particles of the smallest capacity*. These test bodies of smallest capacity must, however, be still large enough to be optically and separately perceived and subjected to physical measurement. We are therefore directed *à priori* to particles whose dimensions correspond with the limiting powers of the microscope. Test bodies of the noble metals or mercury have the special properties of great density and reflecting power which allows them to be individually seen against a dark background down to sizes where other particles are invisible. Moreover, spheres of the noble metals are definitely determined chemically and have, as inert substances, great stability in the inert gases. I have further convinced myself of the sphericity of the test bodies which I used for this purpose. They displayed symmetry against a dark background from all directions and suffered no orientation in an electric field. Furthermore, precipitations of such particles, when resolved with large-aperture microscopes, showed exact sphericity ‡.

Let us consider, say, a mercury sphere of the order of 10^{-5} cm. in an inert gas, nitrogen or argon, and observe it in the gas space between two horizontal metal plates. Let the plates have a diameter of 8 to 9 mm. and be 1 to 2 mm. apart. By suitable arrangements this small space is completely isolated from other gas. Between the plates apply a variable vertical electric field E. The space between the plates is illuminated by the diffuse portion of a beam of light emitted by a horizontally adjusted microscope objective. The observing microscope is adjusted at right angles to this beam. It is then an easy matter to observe against the dark background the uniform speed of this brilliant mercury sphere under the influence of an external force P. In particular, if the test body carries a constant charge e and the field strength in the condenser is E, then the force acting vertically upwards on the body is $e\mathrm{E}-mg$, where

* *Wiener Akad. Ber.* cxix. (ii. *a*) pp. 815–866 (May 1910); *Phys. Zt.* xi. pp. 619–630 (1910).

† *Phys. Zt.* xi. pp. 940–949 (1910).

‡ *Cf.* the tables in the *Wiener Akad. Ber.* cxxiii. (ii. *a*) p. 53 (1914); *Ann. d. Phys.* xliv. p. 664 (1914); *C. R.* clviii. p. 1071 (1914); *Phys. Zt.* xvi. p. 227 (1915); *ibid.* xviii. p. 352 (1917); *Ann. d. Phys.* lvi. pp. 1, 81 (1918); *ibid.* lxiii. p. 773 (1920). For further proofs of sphericity, *cf.* also *Ann. d. Phys.* lvi. p. 54 (1918).

mg is the weight of the mercury particle. It is the limiting steady velocity of such test bodies, attained under the influence of constant external forces in a resisting medium, which we are required to measure as *base* for conclusions. The speed of the test body is proportional to the force acting on it, and hence, in particular, if the force $e\mathrm{E}-mg$ acts vertically upwards the velocity is $(e\mathrm{E}-mg)\mathrm{B}$, where B is the mobility, *i. e.* the speed attained by the body under unit force. The observed speed must, therefore, vary linearly with the field strength if the mobility is actually a constant, and this can, in fact, be demonstrated over wide ranges *.

It remains to define the mobility constant, B, for the test body, and in defining it we also give its magnitude. For this purpose the writer has, up to the present, employed four methods :—

(1) The hydrodynamical method of determining the mobility from the Stokes law of fall for spheres in resisting gaseous media. This is the classical method by which J. J. Thomson and his school determined the size of a falling "cloud" particle. At the Science Meeting in Königsberg (1910) I drew attention † to the fact that in this case Cunningham's correction has to be applied ‡.

(2) An optical determination § of the magnitude of the particle and with it the mobility. To this end the writer observed the colour of the light scattered. For these bodies are small enough for individual selective colouring to be visible in the microscope : in general, the smaller the sphere the shorter is the wave-length of the perpendicularly diffracted light, though the colour of this diffracted light depends also upon the optical constants of the sphere. If, therefore, we calculate the colour of the light radiated from a sphere of known size, we can deduce the size of the test body from its observed colour.

(3) The writer could also determine the size and mobility from the photophoretic maximum ‖ of the forces acting on a silver particle. We assume in this that the positive photophoretic force of light on silver is identical with the light pressure. I have already shown ¶ that small test bodies in

* *Ann. d. Phys.* lxiii. p. 782 (1920).

† *Phys. Zt.* xi. p. 952 (1910) ; *Wiener Akad. Ber.* cxix. (ii. *a*) p. 860 (1910).

‡ See Fritz Zerner, *Phys. Zt.* xx. p. 546 (1919).

§ F. Ehrenhaft, *Phys. Zt.* xv. p. 952 (1914); xvi. p. 227 (1915), etc.

‖ *Phys. Zt.* xviii. p. 367 (1917).

¶ F. Ehrenhaft, *Ann. d. Phys.* lvi. p. 81 (1918): "Die Photophorese."

gases are driven either with the light, "light-positive," or against it, "light-negative." The discussion of the nature of these forces is by no means at an end. Assuming, however, that the light-positive action on silver, which has a high reflective power, arises from light pressure; since light pressure for certain spheres must be specially strong *, we can draw conclusions regarding the size of these spheres from observations of the maximum action.

(4) Finally, the mobility † can also be deduced from the Einstein theory ‡ of the Brownian movement in gases §. This method seems to the writer, however, the most untrustworthy of all inasmuch as it gives results differing ‖ from those of the other three, while the latter are self-consistent.

From the very first I found charges on individual test bodies, from metals as well as from mercury, which were often only small fractions of the so-called elementary quantum of electricity. The general conclusion was reached that test bodies below a radius of 3×10^{-5} cm. often carry charges smaller than that of the electron and, hence, that the charge on test bodies decreases ¶ on the average with their capacity (and hence radius). In this connexion charges of the order of a tenth or twentieth part of the electron's are by no means the smallest.

The most serious objection raised against this result, which contradicts the prevailing theory, has been that the test bodies which I used were not spheres; but this is, of course, sufficiently met by microphotographs and direct observation, if, indeed, one is inclined at all to doubt determined sphericity in the case of minute mercury particles **.

A further objection has been that the density of the test body was not that of the molar (bulk) substance. Under the high-power microscope, however, the spheres still show the colour and glitter of the molar substance. Nevertheless,

* See P. Debye, *Ann. d. Phys.* xxx. p. 57 (1909).

† E. Weiss, *Wiener Akad. Ber.* cxx. (ii. *a*) p. 1021 (1911); F. Ehrenhaft, *Verh. d. deutsch. phys. Ges.* xv. p. 1187 (1913), etc.

‡ E. Einstein, *Ann. d. Phys.* xvii. p. 549 (1905); xix. p. 371 (1906).

§ F. Ehrenhaft, *Wiener Akad. Ber.* cxvi. (ii. a) p. 1175 (1907).

‖ Cf. *Ann. d. Phys.* lvi. p. 71 (1918); S. Landman, *Zt. f. Physik*, xxvii. p. 237 (1924).

¶ Cf. *Phys. Zt.* xii. p. 103 (1911).

** M. A. Schirmann has recently in my department (*Phys. Zt.* xxiii. p. 441, 1922) investigated light polarized by diffraction from submicroscopic particles of Hg, Au, Cu, Pb, oil, and a modification each of S, Se, and Te, which were still smaller than the above test bodies, and has shown their complete symmetry for all orientations.

the quite implausible assumption has been made that the density of platinum (21·4) or mercury (13·56) could vary from particle to particle and in the case of platinum, for example, sink * to 0·2. Such assumptions are actually necessary if the charge $4{\cdot}774 \pm 0{\cdot}004 \times 10^{-10}$ e.s.u. is to be accorded to individual test bodies.

As a third objection it has been maintained that the test bodies are surrounded by gas layers † resulting in the deduction of wrong charges. This hypothesis also seems untenable, for with modern methods of investigation in this region, carried out, it is granted, on matter in bulk, the contrary conclusion was reached, viz. that no gas layers are found to any extent that matters. At the most we find layers of the order of one molecule ‡ thick. It is, further, impossible to imagine what forces could cause gas layers great enough to influence the results.

Finally, it has often been emphasized that the exact form of the law of resistance for such small spheres in a gas (*e. g.* Stokes, Stokes - Cunningham, Knudsen - Weber, Millikan, Zerner, Lenard, Epstein) is not yet known. We must, of course, keep in mind that if, on the one hand, the validity of the resistance law for small moving spheres of mercury and other material is to be doubted, then it cannot hold, either, for other substances, *e. g.* oil. The withdrawal of such a premiss would of course cut the ground away from the elementary quantum idea of $4{\cdot}774 \pm 0{\cdot}004 \times 10^{-10}$ e.s.u. as deduced from observations of electric charges on individual oil drops on the assumption of the validity of one of these laws. The writer, however, has all along taken the stand that an exact and purely empirical derivation of the resistance law for small spheres falling in a gas, which has hitherto been only theoretically formulated or found by observations on large spheres, is still to be attained. At the same time, we must take care that the experimental derivation of this resistance law does not contain the presupposition of an indivisible electron, as has been done in the well known work of R. A. Millikan. Such a procedure is a case of *petitio principii*. No significance can therefore be attached

* R. Bär, *Ann. d. Phys.* lxvii. p. 193 (1922). Against this, *cf.* Th. Sexl, *Wiener Akad. Ber.* cxxxii. (ii. *a*) p. 139 (1923); *Zt. f. Physik*, xvi. p. 34 (1923); *Zt. f. Physik*, xxvi. p. 371 (1924).

† *Cf.* my remarks in the discussion at the Science Meeting in Nauheim, *Phys. Zt.* xxi. p. 624 (1920).

‡ *Cf., e. g.*, T. Langmuir, Journ. Amer. Chem. Soc. xl. p. 1361 (1918); F. Paneth, *Zt. f. phys. Chemie*, ci. pp. 445, 480 (1922); *Zt. f. Electrochemie*, xxviii. p. 113 (1922); *Zt. f. angew. Chemie*, xxxv. p. 549 (1922).

to resistance laws derived in this manner from which in turn the electronic charge is deduced, its existence, of course, being by such methods easily demonstrable. The exact determination of a resistance law must follow from a method which is completely free from any assumption of the existence or non-existence of an elementary quantum, as well as of the divisibility or indivisibility and also of the equality of charge on the various drops. Such an investigation has long been going on in this Institute and is nearly completed. The purely mechanical and experimental determination of the correction to be applied to Stokes' law for the motion of a small sphere in a gas has thus not as yet been realized. It is, however, to be remarked that the final result of the experiments which are discussed below is independent of the exact numerical value of the quantity *

$$B = \left[1 + \frac{l}{a}(A + De^{-C\frac{a}{l}})\right] / 6\pi\mu a.$$

On the other hand, it is important to demonstrate for later deductions that the electric field is of uniform strength and direction at all points between the plates of the condenser. An ideal *ballon-sonde* for investigating the field is a test body of the order of 3×10^{-5} cm., say a mercury sphere of constant charge, for it is infinitely small as compared with the length of path observed and the condenser dimensions. It turns out that this test body is driven with constant speed † and direction in all parts of the field. Whence it follows that the field is completely constant at all points of the condenser, and the *proviso* of a homogeneous field is satisfied.

Such a colloidal test body with constant charge may even be used as an electrometer, for it is easily found that it rises with uniform speed in a field of constant gradient. If, however, we suddenly cut off the voltage from the condenser plates the upward motion becomes less and less, the body finally stops, turns about, and begins to fall with acceleration. This procedure can be repeated indefinitely on the same test body, and the reason for the phenomenon is quite clear. When the plate tension is cut off the condenser charge passes through

* l, mean free path of the gas molecule.
μ, coefficient of internal friction for gases.
a, radius of test body.
A, D, C, constants.

† *Cf.* F. Ehrenhaft and D. K. Konstantinowsky, "Radioaktivität und Elektrizität," *Ann. d. Phys.* lxiii. p. 780 (1923).

the ebonite insulation of the container and is dissipated outside. In this way the potential difference varies and with it the field between the plates. The magnitude of the field is given at every instant by the speed of the test body. The electric force acting on it is at first still greater than its weight and so it rises with continuously decreasing velocity. These forces ultimately become equal and the body halts. Then the electric force is exceeded by gravity and the body falls with increasing speed. We thus see that in such experiments the test body assumes the function of an electrometer, for it enables us to calculate easily the tension on the condenser plates from the velocity observed.

It can thus be seen from these details that such a colloidal particle makes an ideal instrument for determining the quality and direction of the field, and, finally, that knowing the capacity * of the condenser in which it serves as electrometer, information is given as to the condenser's rate of leak.

A test body possesses, in general, a mean constant rate of rise or fall in a field of constant strength, and from this we deduce that it also possesses constant mass and charge. If we vary the charge on the test body at any time, it is well to remove the electric field for an instant and at the same time ionize the gas between the condenser plates by outside means (radium preparations, Röntgen rays, ultraviolet light, etc.). On reapplying the field the motion of the same test body is again observed. It is then often found that a new velocity, in the same or the opposite direction, has been acquired, so that a variation of charge on the test body is deduced from the change in velocity. The charge on the particle is then said to have been varied from outside.

§ 3. In 1909 I set myself the problem of measuring the electric charge on the smallest possible individual particles and thereby subjected the foundations of the electron theory to a sharper test. Similarly the present problem is to follow, if possible, radioactive phenomena not statistically, as done hitherto, but observing the detail of the time variation of the radioactive process itself. I have succeeded † in doing this by investigating the motion of a small colloidal spherical

* Cf. *Ann. d. Phys.* lxiii. p. 792 (1920).

† These and the following investigations were carried out with Dr. D. Konstantinowsky, who was my assistant at that time.

test body, which was radioactive and of dimensions of the order of 10^{-5} cm., in a constant electric field.

The first thing to do was, thus, to transform small test bodies of these dimensions into a radioactive condition. As is well known, the writer has been able to form spherical particles of any substance, *e. g.* mercury or selenium, by vaporization. Radioactive particles can also be formed in this manner. For this purpose, radium emanation was enclosed in a vessel with selenium powder or mercury and the vessel was shaken for several hours, so that the break-down products of the radium emanation—radium A to radium D—were shaken out upon the substance used. The excess emanation was removed and the infected substance brought into another chamber (a small bulb) *. To remove all remains of the emanation that might have been occluded, the bulb and contents were heated and at the same time dry pure gas allowed to pass through it. Such test bodies must necessarily emit radiations of all kinds (α, β, γ, δ) on account of the radioactive substances produced. To obtain, further, a radiation of α rays only, we separated out electrolytically polonium on selenium. The selenium was actually found to be a radiator of α rays only.

It is now possible by suitable arrangements † to bring a single one of these test bodies between the plates of my condenser and subject it at once to measurement. The very first one showed a quite different behaviour from that of the non-radioactive particles. The movement in the constant electric field was no longer uniform, and the particle often changed from one type of motion to another with accompanying change of speed, giving one completely the impression of a continuous change of electric charge.

We must therefore next follow the phenomenon quantitatively by registering the velocity of the test body as nearly continuously as possible. The times required by the falling particle to pass successive scale-divisions of the observing microscope were recorded. The field was then so altered that the same particle rose past the same divisions, at the same point in the condenser. The change of field in the condenser was brought about in such a way as always to have a voltage difference on the plates. The test body was thus at no time in a field of no gradient. The following figures give some idea of what happens :—

* Cf. *Ann. d. Phys.* (4) lxiii. p. 813 (1920).
† Cf. *loc. cit.* p. 787.

Fig. 1.

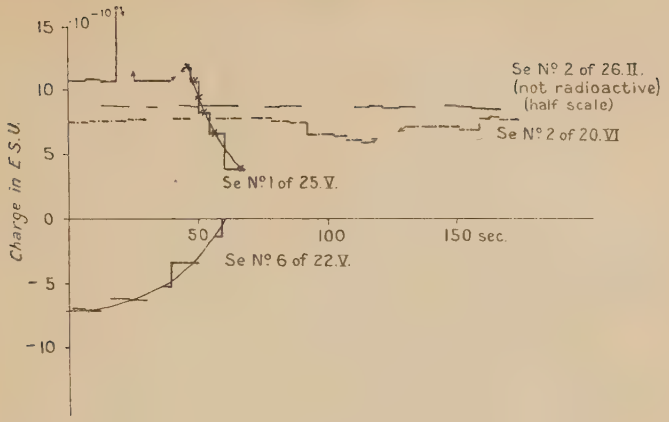


Fig. 2.

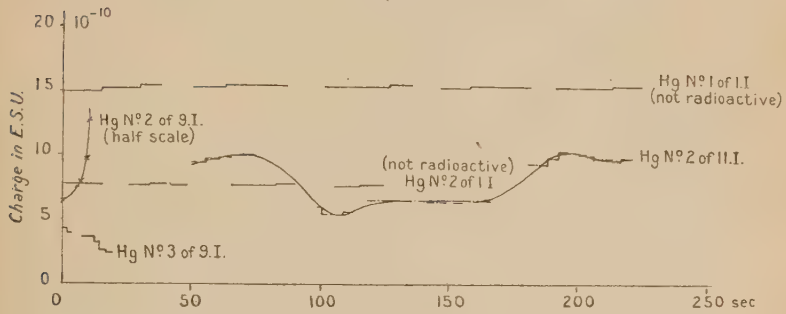


Fig. 3.

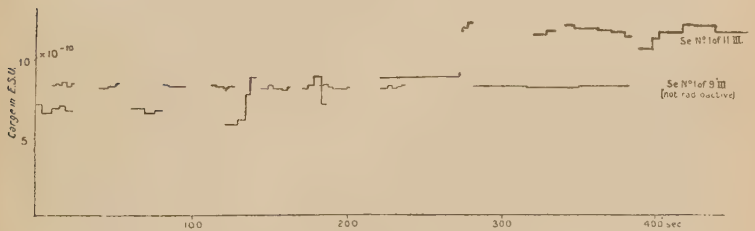


Fig. 4.

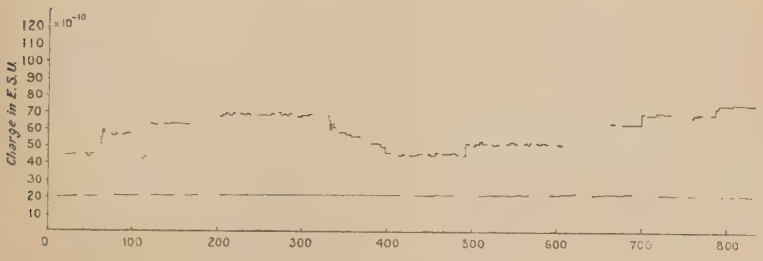


Fig. 4 *a*.

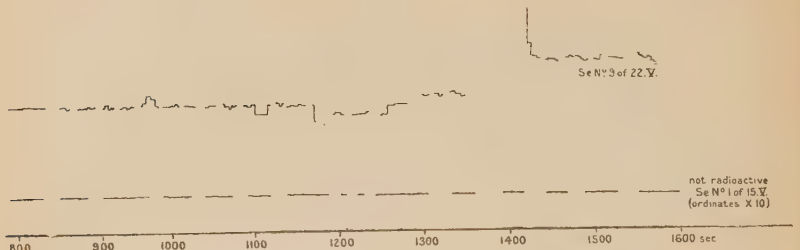


Fig. 5.

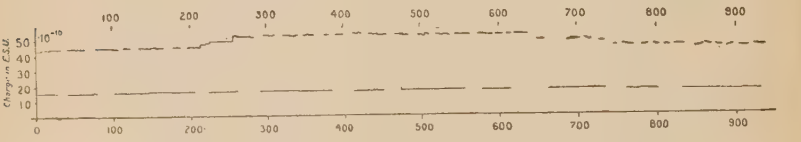
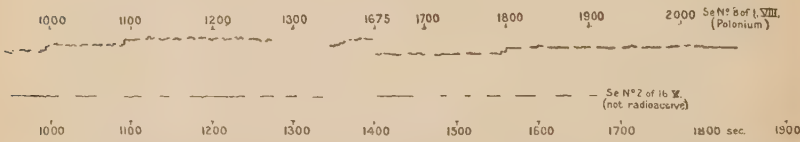


Fig. 5 *a*.



In the above figures the average charges are plotted as ordinates against the times as abscissæ ; the individual points corresponding to continuously varying charges cannot be determined, but only the average values of the charges during the periods of rise or fall while the test body passes a few successive divisions of the eyepiece scale. Non-radioactive test bodies were introduced as a check, and fit extraordinarily well along a straight line parallel to the abscissa axis. The minute variations of these step curves are sufficiently accounted for by observational errors. The charges on the test bodies sometimes vary extraordinarily—sometimes in shorter, sometimes in longer periods. For example, the selenium particle no. 1 of May 20 (fig. 1) after about 20 seconds shows an apparent abrupt variation in charge of about 6×10^{-10} e.s.u., followed immediately by a return to the original positive charge of a little over 10×10^{-10} e.s.u. It retained this charge for about 20 secs., gained a small amount during the next half-minute, and then lost it gradually down to about 3×10^{-10} e.s.u. Readings were taken five times during this latter loss of charge. A second particle (selenium no. 6, May 22, fig. 1) lost its charge of

about -7×10^{-10} e.s.u. in a minute, and so on. It, too, was recorded five times. The particle mercury no. 2 of Jan. 9 (fig. 2) varied in charge continuously over some ten seconds from about 13×10^{-10} e.s.u. to, say, 25×10^{-10} e.s.u., and was recorded five times during this continuous increase. The charge on the particle mercury no. 2, Jan. 11, varied continuously between about 10 and 5×10^{-10} e.s.u. We must keep in mind, here, that these test bodies had been in contact with emanation and would therefore emit all four radiations α, β, γ, δ. A similar condition of affairs (*vide* figs. 3, 4, 4 *a*) is furnished by the particles, selenium no. 1 of Mar. 11, and selenium no. 9, May 22. The latter was under observation for 1600 secs. These variations should be compared with those under similar conditions and shown in the same figures, but given by the non-radioactive particles selenium no. 1 May 15, and selenium no. 1 March 9. On the other hand, the particle selenium no 3 Aug. 1 (figs. 5, 5 *a*) contained only polonium. It was observed over 2000 secs., showing seven slow continuous changes in charge and only one more rapid change. It could only be expected to emit α-particles. It is to be noted, in particular, that a series of test bodies observed over relatively long periods of 10 to 50 secs. showed an apparently continuous loss of charge, *e. g.* from 10 to 5×10^{-10} e.s.u. and from -7×10^{-10} e.s.u. to zero.

It might be objected here that the absolute charge on these test bodies is still somewhat indeterminate, since the question of determining the body's size from its velocity under gravity is not yet finally cleared up. For, as mentioned at the beginning, the purely mechanical determination of the correction term in the resistance law for small spheres falling in a gas is still to come. From the previous discussion, however, it is clear that the question turned rather on the exact determination of a small correction term. As regards deductions from these experiments such a question is of no importance, for when a particle loses its charge continuously in about 60 secs. from -7×10^{-10} e.s.u. to zero and is meantime eight times observed, it is all the same whether the absolute value of the charge at the beginning of the run was -7 or -6 or -8×10^{-10} e.s.u.

We must now ask whether these new phenomena can be explained without either having to make the assumption of charges smaller than those of the electron or subscribing again to the old idea of continuity in electricity. We calculated, for example, the impulse which would be given

to the test particle by the ions imagined to have been generated by the impact of an α-particle and accelerated by the field, but it was found to be 10^6 times too small * to be at all observable. Static space charges cannot exist between the condenser plates, as there is always a high gradient (1 to 4 e.s.u./cm.), and it is only the test body which remains, owing to the suitable field regulation.

From this discussion it follows that the phenomenon of continuous charge variation on radioactive test bodies cannot, in my view at least, be regarded otherwise than as due to the fact that such small particles are capable of picking up or losing charges which are only quite small fractions of the supposed indivisible electronic charge. This is in agreement with the point of view I have represented for 16 years, that minute test bodies are frequently observed with charges which are to a different order of magnitude smaller than the electric charge.

The above results seem similar to those of Kapitza mentioned at the beginning, but it must be borne in mind that they were observed in a field of high potential gradient, so that they can no longer be explained by capture and loss of free electrons in the gas.

During the last three decades a series of phenomena have been observed in Physics which lead ultimately to the decision that the indivisible atom has to be broken up into smaller parts. What was considered indivisible up to a certain point, in time falls a victim at last to division. The case seems quite the same with the electron. There may be a group of phenomena capable of seeming explanation on the assumption of preferential charges. On the other hand, it does not seem justifiable under any circumstances to conclude that only certain preferred charges occur, *i. e.* are universal, all other conditions of charge being excluded. It is especially not clear why observations on individual charges should not show smaller charges, nor why the separate electrons cannot also be split up in the midst of such mighty energy changes as accompany radioactivity. And this is all the more true, since, as far as the writer is aware, there is up till now no theory of any kind to account for the electron's cohesion. A number of well-known investigators, such as Poincaré, Weyl, Einstein, etc., have raised the question of the electron's stability. No conclusion has been reached. This very question, however, implicitly contains the possibility of a break up. The point of view that the electron is in all cases strictly indivisible

* Cf. *loc. cit.* p. 790.

would place the question as to its stability among the superfluous. No investigator has so far, however, as far as I know, taken this stand.

I have to thank Mr. Herbert Bell, of Manchester University, for his great kindness and trouble in translating this article from German into English.

The University of Vienna,
December 1923.

Appendix.

An important advancement toward the purely experimental determination of a law of resistance in the sense indicated above, without the presupposition of the electron, has since been made in my department through the work of J. Mattauch, *Phys. Zt.* 1924. From observations of the same test-body under different gas-pressures, he succeeded in establishing a law of resistance, or in confirming the Knudsen-Weber law. I cite this although, as already mentioned, this circumstance is irrelevant as regards the conclusions of this paper. Further, important points concerning the nature of the different test-bodies might be obtained from the photoelectric properties of those individual test-bodies which, on illumination with ultraviolet light, very frequently give off positive charges (and indeed by fractions of the electron) and not exclusively negative ones as one might expect from the theory. (*Cf.* M. Hake, *Zt. f. Phys.* xv, p. 110, 1923, and E. Wasser, *Zt. f. Phys.* xxvii. p. 203, 1924.) However, departures from the elementary quantum must also have been observed in the researches of the Millikan school, for Ishida writes (Phys. Rev. xxi. p. 550, 1923): "There were a few cases that had to be discarded, the results being for some unexplained reasons 10 to 50 per cent. out." Silvey likewise communicates (Phys. Rev. vii. p. 87, 1916): "As a rule, however, the more slowly falling particles indicating no evaporation, gave values for the ultimate charge much lower than if they had been pure mercury droplets with the same speed under gravity, although the change in charge was an exact multiple of the charge originally on the droplet." As is known, Millikan uses the mercury droplets observed by Derieux besides oil as a second experimental material for the determination of the electron. Th. Sexl (*Zt. f. Phys.* xxvi. p. 371, 1924) has shown that these give results departing from the elementary quantum provided one computes with the law of resistance consistent with the mechanical conditions (*i. e.* determined by the velocity of fall of the same test-body under different gas-pressures). *The discrepancy appears to lie, therefore, not at*

all in the observations but in the interpretation of the experimental results.

The University of Vienna,
December 6th, 1924.

[Since the war period inevitably perturbed the interrelations between Austrian and American science, it seems fair to allow space for Professor Ehrenhaft's contention about the fundamental unit of electric charge, which he regards as not an indivisible unit. But it is also fair to Professor Millikan to point out that in his book, 'The Electron,' published in 1917, he devoted a long chapter to a discussion, and what he considered a refutation, of Professor Ehrenhaft's contention that the existence of fractions of an electronic charge were demonstrable:

(1) by criticism of statistical methods,
(2) by the Brownian movement,
(3) by direct observation of microscopic silver particles in a horizontal electric field.

Professor Millikan's own words, near the end of Chapter VIII., are as follows:—

> "While then it would not be in keeping with the spirit or with the method of modern science to make any dogmatic assertion about the existence or non-existence of a sub-electron, it can be asserted with entire confidence that there is not in Ehrenhaft's experiments a scrap of evidence for the existence of charges smaller than the electron. If all of his assumptions as to the nature of his particles are correct, then his experiments mean simply that Einstein's Brownian-movement equation is not of universal validity, and that the law of motion of minute charged particles is quite different from that which he has assumed. It is very unlikely that either of these results can be drawn from his experiments, for .... [certain verifications of the law have been given] ..... I have thus far found no evidence of a law of motion essentially different from that which I published in 1913.
>
> "There has then appeared up to the present time no evidence whatever of the existence of a sub-electron."

The last sentence is printed by Prof. Millikan in italics.

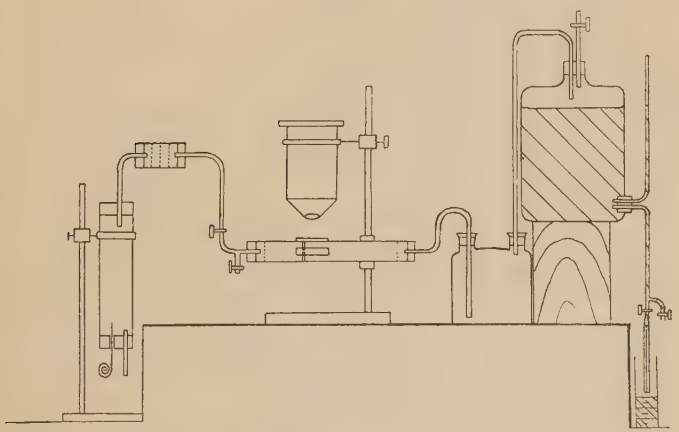
Nevertheless the fundamental importance of the atomic nature of electricity, and the size of its ultimate unit, is so great that no serious attack on the orthodox position can be ignored. O. J. L.]

LXIX. *On Eddies formed behind Apertures through which Air is Streaming.* *By* A. L. Griffith, *B.Sc.*, *and* Alfred W. Porter, *D.Sc.*, *F.R.S.* *

THE work described in this paper is complementary to that on "Eddies in Air" (Phil. Mag. xlvi. p. 754) by Nisi and Porter, since it deals with apertures in plates instead of obstacles.

The flow of gas took place in a cylindrical metal chamber, of square section, divided by a transverse metal frame in which the plates containing the apertures were successively fitted. The complete apparatus is sketched in fig. 1.

Fig. 1.



Arrangement of Apparatus and Experimental Description.

Water flows from a ten-litre aspirator and causes a suction which draws air through the whole apparatus. The air first enters a large chamber in which smoke is produced. This smoke is picked up by the air, and carried along through a smaller chamber containing three gauze obstacles which stop the heavier and larger smoke particles and steady the general flow. The smoke-laden air now passes into the observation chamber. This consists of a square-section brass tube

* Communicated by the Authors.

containing at each end a fine gauze to steady the flow, and, one-third along its length, a diaphragm in the middle of which is the aperture to be experimented with.

Two sizes of observation chamber were used—the smaller $2{\cdot}6 \times 2{\cdot}6 \times 30$ cm. and the larger $5 \times 5 \times 30$ cm., with aperture varying from ·25 cm. to ·05 cm.

In the middle of the observation chamber, windows were cut in the sides and top, and these were covered with thin glass plates. Horizontal illumination was provided by a 5–10-amp. carbon arc, the light from which was focussed by suitable lenses into a thin horizontal sheet in the axial plane of the chamber in the neighbourhood of the diaphragm, heat-filters being employed to reduce the heating effect of the arc to a minimum. After passing through the observation chamber, the air traverses a five-litre vessel which minimizes any tendencies towards pulsations in the gas-flow. Thence it passes to the aspirator.

The phenomena were observed vertically by the light scattered by the smoke particles being focussed by a camera lens of wide angle and short focal length. The image of the smoke was focussed on a graduated ground-glass screen which, if necessary, was replaced by a photographic plate, and a photograph taken.

At first, horizontal flow and horizontal observation were used, but the latter had to be abandoned because the gravity effect on the smoke cloud produced dissymmetry in the field of view. The lower part of the field contained the larger particles, which had settled owing to gravitation, and the photographic exposure necessary for these was very different from that required by the upper part.

Various kinds of smoke were tried (*e. g.*, tobacco smoke, powdered silica, ammonium chloride, and magnesium oxide), but magnesium oxide was used for most of the observations. Typical cases were photographed, but in the majority of cases eye observations only were taken.

The flow of water from the aspirator was controlled by a system of capillary tubes, and the mean velocity of the gas in the aperture was calculated from the rate of flow of water from the aspirator. This rate of flow was measured by means of a graduated tube and a stop-watch.

The room temperature was noted each day of experiment, and it was found that the slight daily variations of temperature had an inappreciable effect on the experiments.

Notation.

Throughout this paper the following notation is used :—

d, diameter of aperture.
D, diameter of observation chamber.
Z, longitudinal distance from diaphragm.
X, transverse distance from axis of chamber.
y, mean velocity of gas in aperture.
y_c, mean critical velocity of gas in aperture.
v, longitudinal velocity of gas in chamber.
w, transverse velocity of gas in chamber.

Part I.

The Relation between the Dimensions of the Apertures and the Critical Velocities.

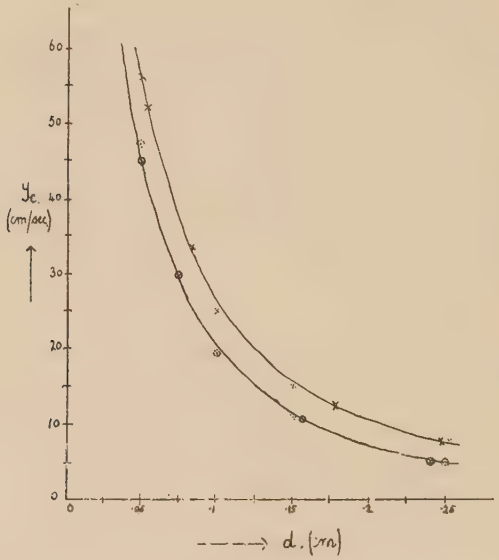
It was found on first using the apparatus described, that on varying the gas velocity three distinct types of motion occurred. First of all a steady stream-line flow of the gas through the aperture is seen ; then, as the velocity increases this stream-line flow ceases, and a steady eddy motion takes place, the centres of the eddies formed having fixed positions in the chamber. Lastly, as the velocity is increased still further, the eddies are no longer stationary, but move down the tube as soon as they are formed.

The critical velocities studied were (1) those between stream-line flow and steady eddy motion, and (2) those between steady eddy motion and unsteady eddy motion. Each aperture is in reality a short tube of length equal to the thickness of the plate. Four such cylindrical tubes were used successively in each chamber. The diameter of these apertures ranged from ·05 to ·25 cm. Each critical velocity was measured both when the velocity was being increased and when it was being diminished. This was repeated several times, so that each critical velocity was determined six to ten times. The temperature of the air-stream was noted in each case, magnesium oxide being the smoke used. In all this work it was found necessary to use a somewhat long heat-filter and a small light stop, in order to render the heating effect negligible.

The critical velocities determined from observations of

the moving particles were plotted as graphs against the diameters of the apertures (figs. 2 and 3).

Fig. 2.



Critical Velocity between Stream-line Flow and Steady Eddy Motion.

×	Large Chamber.	Experimental Points.
⁘	do.	Points from Formula.
⊙	Small Chamber.	Experimental Points.
◌	do.	Points from Formula.

Each critical velocity gave one curve for each tube, all of the same general shape, the pairs of curves for the two types of critical velocity being of somewhat similar shape, although we have not found it possible to represent both by similar algebraic equations.

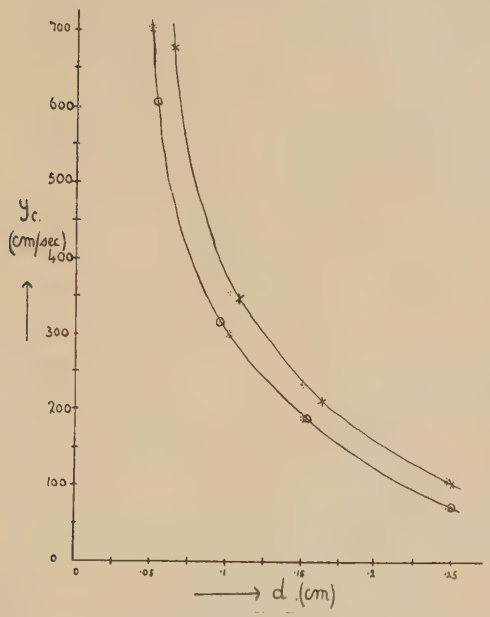
Various types of equations were tried for these curves, but the best results were obtained using an equation of the general form

$$v_c = \mathrm{A}\frac{\mu}{\rho d}\left[1+\mathrm{B}\left(\frac{d}{\mathrm{D}}\right)\right]^n,$$

which is dimensionally correct if A and B are numerics.

In the case of critical velocity between stream-line motion and steady eddy motion $\mathrm{A}=20{\cdot}1$, $\mathrm{B}=12$, and $n=-1$, while

Fig. 3.



Critical Velocity between Steady Eddy Motion and Unsteady Eddy Motion.

×	Large Chamber.	Experimental Points.
⁘	do.	Points from Formula.
⊙	Small Chamber.	Experimental Points.
◌	do.	Points from Formula.

for that between steady eddy motion and unsteady eddy motion $A=270$, $B=-4{\cdot}2$, and $n=3/2$. It must be clearly understood that such a formula as the above can only hold for small values of d/D.

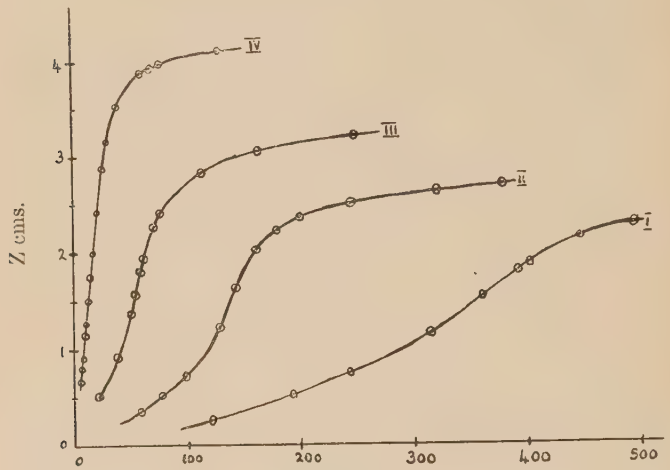
Part II.

The Distances of Eddy Centres from the Plane of the Aperture.

The same four cylindrical tubular orifices were used in each chamber, and the longitudinal distances of the eddy centres from the diaphragm were measured for velocities in the aperture varying continuously from the critical velocity at which stream-line flow ceases and steady eddy motion begins, to the critical velocity at which steady eddy motion ceases and unsteady eddy motion begins.

On plotting the longitudinal eddy distances against the mean velocities of the gas in the aperture, each chamber gave a system of four curves (figs. 4 and 5).

Fig. 4.

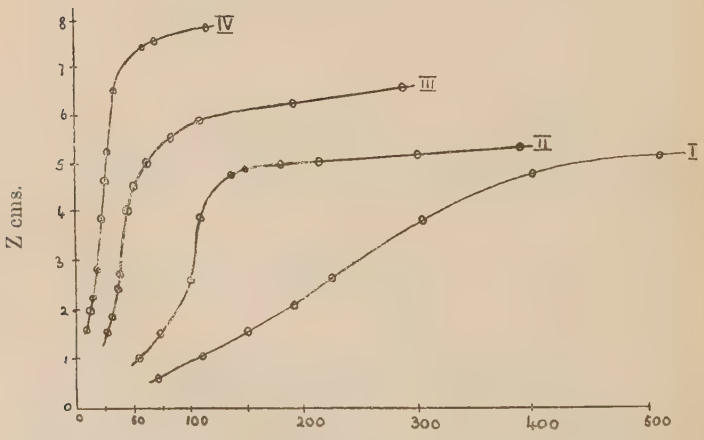


y (cm./sec.).

Tubular Apertures in Small Chamber.

I. d=·052 cm. II. d=·079 cm. III. d=·159 cm. IV. d=·238 cm.

Fig. 5.



y (cm./sec.).

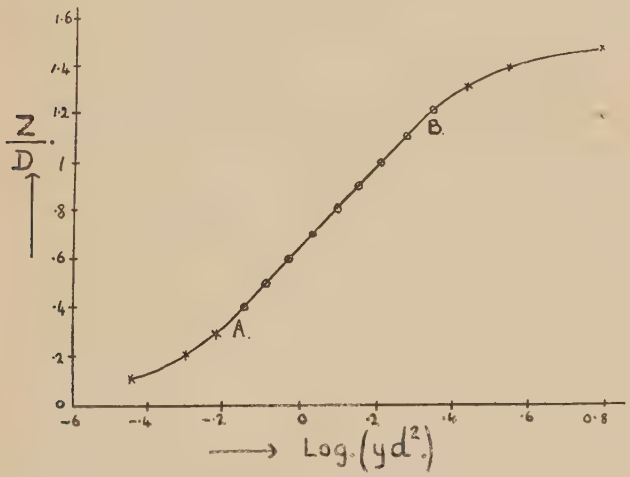
Tubular Apertures in Large Chamber.

I. d=·052 cm. II. d=·079 cm. III. d=·159 cm. IV. d=·238 cm.

The eddy distance divided by the diameter of the chamber was now plotted against the mean gas velocity in the aperture, and it was found that the curves corresponding to the two chambers coincided.

In order that the variable quantities might be further connected, the quotient of the eddy distance and the diameter of the chamber was plotted against the product of the mean gas velocity in the aperture and the square of the diameter of the aperture; *i. e.*, $\frac{Z}{D}$ against yd^2.

Fig. 6.



AB is Period of Steady Eddy Motion.

In this way the original eight curves were reduced to one curve. A final graph was now drawn in which the logarithms of the previous abscissæ were taken as the new abscissæ. The resulting curve (fig. 6) can be divided into three definite parts :—

I. Velocities less than for steady eddies.

II. Steady eddy motion where $\frac{Z}{D} \propto \log yd^2$.

III. Velocities greater than for II.

For the second part of the curve, which corresponds to the greater part of the experiments (*i. e.*, steady eddy motion) $\frac{Z}{D} \propto \log (yd^2)$, as shown by the straight-line part of fig. 6.

For this part of fig. 6,

$$\frac{Z}{D} + \log A = K \log (yd^2),$$

where A must have the dimensions of (yd^2) and K is a numeric.

Part III.

Velocity Distribution in the Eddies.

In order to study the velocity distribution in the eddies when they were formed, very short exposure photographs were taken, using a full aperture lens and intense illumination. Owing to the difficulties of photography, these were only taken of typical cases. Great care was necessary to obtain successful photographs uniformly illuminated and corresponding to absolutely steady flow. The camera was clamped to a slate bench in order to obtain complete rigidity.

Each smoke particle appears on the photograph as a line, the direction and length of which represent the direction and magnitude of the velocity in the corresponding region of the eddy.

The exposure used was of the order of one-tenth of a second, and of course was varied with the velocities of the eddies, in order to keep the streaks of the photograph to reasonable dimensions and prevent overlapping.

The photographs when obtained were projected, using an ordinary lantern, on to squared paper, using a magnification of about ten times.

The streaks of the image represent the resultant velocities in both direction and magnitude.

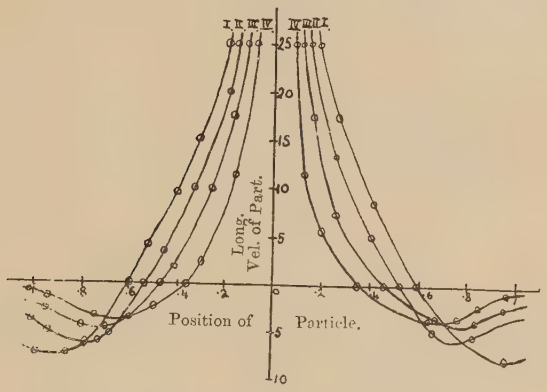
The rectangular components of these were measured, and thus the longitudinal and transverse velocity distributions in the eddies were obtained.

These two velocity components were plotted against the position of the particles in the eddies, using the axis of the chamber (which passes through the aperture) and the line joining the eddy centres as reference axes.

The space between the eddy centres and the diaphragm was divided into four equal spaces by transverse lines drawn at right angles to the axis of the chamber, and the two velocity components along these lines were plotted separately against the position of the particle in the eddies (figs. 7 and 8). The case shown is that of the phenomenon in the

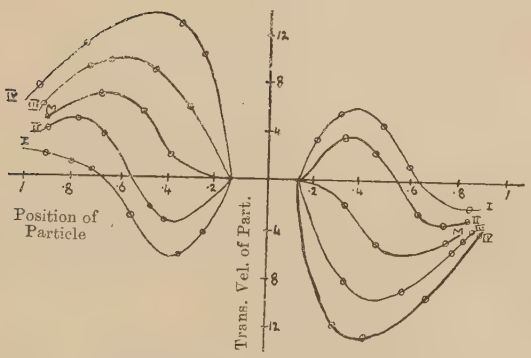
smaller chamber at a mean gas velocity in the aperture of 50·6 cm./sec. In the case of the transverse velocity components, an extra section (M) was included midway

Fig. 7.



Longitudinal Velocity Distribution.

Fig. 8.



Transverse Velocity Distribution.

between the others to show the gradual transition in the shape of the curves.

Mathematical equations of a two-term exponential type were fitted on to the family of longitudinal velocity distribution curves, using the method of Sir J. J. Thomson (Phil. Mag. xxx. p. 780, 1915).

The equations determined were :—

Curve I. ..... Z=·973 cm. $v=61{\cdot}52\,e^{-5{\cdot}26(X)^2}-14{\cdot}48\,e^{-{\cdot}887(X)^2}$

Curve II. ..... Z=·730 cm. $v=59{\cdot}17\,e^{-7{\cdot}52(X)^2}-10{\cdot}57\,e^{-{\cdot}829(X)^2}$

Curve III. ..... Z=·487 cm. $v=57{\cdot}48\,e^{-10{\cdot}34(X)^2}-7{\cdot}41\,e^{-{\cdot}818(X)^2}$

Curve IV. ..... Z=·243 cm. $v=56{\cdot}08\,e^{-14{\cdot}88(X)^2}-6{\cdot}02\,e^{-{\cdot}682(X)^2}$

The values of X and D were 1·28 cm. and 2·54 cm. respectively.

It will be seen that the index of the first term on the right of each equation varies inversely as Z, whereas that of the second term is at any rate approximately independent of Z. Hence a single equation which will approximately represent all the cases is :

$$v=59\,e^{-4{\cdot}84\left(\frac{X^2}{Z}\right)}-17{\cdot}4\,Ze^{-{\cdot}80(X)^2},$$

where the numbers in the indices must vary inversely as a length and a square of a length respectively. The factor 59 must have the dimensions of a velocity, and the factor 17·4 must have the dimensions of $\left[\frac{1}{T}\right]$. The determination of the way in which they depend on μ, ρ, d, and D requires further experimental examination.

Part IV.

Interaction of Neighbouring Apertures.

The effect of one aperture being near another was now experimented upon. Diaphragms containing pairs of tubular apertures of ·159 cm. diameter, separated by different distances, were placed successively in the larger observation chamber, and the longitudinal distances of the eddy centres for varying mean velocities of the gas in the apertures measured.

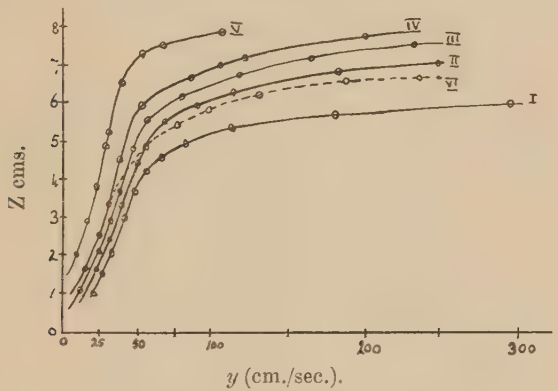
These two quantities were graphed as before (fig. 9) and deductions made from the curves obtained.

The eddies were observed along the line of centres of the pair of apertures, and it was found that the eddy centres' distance was in all cases greater than for a single aperture, and less than the distance for a single aperture of the same area as the sum of the areas of the two apertures and for the same aperture velocity.

The eddies were also observed at right angles to the line of centres of the apertures ; and in this case it was found

that, for slow velocities of the gas in the apertures, the eddies were the same distance as in the line of centres, but as the aperture velocity of the gas increased, the two curves separated, though having the same general shape. At right angles to the line of centres of the apertures also, the eddy-centre distance was always greater than the corresponding distance for a single aperture.

Fig. 9.



Interaction of Neighbouring Apertures.

I.	One Aperture.	·159 cm. diam.		
II.	Two Apertures.	·159 cm. diam.	·953 cm. apart.	
III.	do.	do.	·635 cm. apart.	
IV.	do.	do.	·318 cm. apart.	
VI.	do.	do.	do.	[⊥ to line of
V.	One Aperture.	·238 cm. diam.		centres.]

As a general result it was found that when two apertures are separated by eight or nine times their diameter, the effect of one aperture on the other is very small.

Part V.

Cylindrical Apertures of Elliptical Cross-Section.

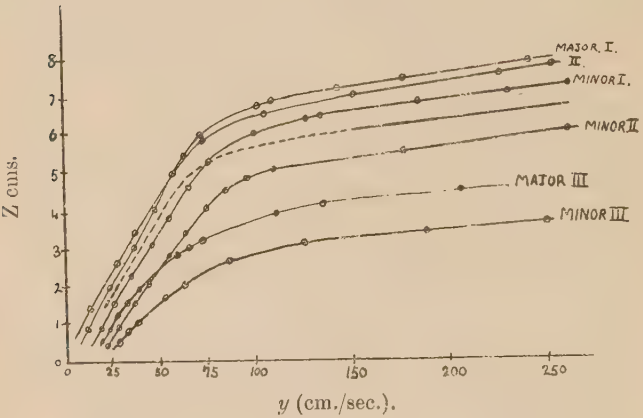
The eddies formed by cylindrical apertures of elliptical cross-section were now examined. Three elliptical apertures were made for the larger observation chamber, each having the same area as a cylindrical aperture of circular cross-section of ·159 cm. diameter, and having as ratios of their major to their minor axes the numbers 1·66, 4, and 10.

The eddies which formed, and the mean longitudinal eddy-

centre distances, were measured along their major and minor axes for corresponding mean velocities of the gas in the apertures, and the results expressed as before (fig. 10).

The distances measured longitudinally in the plane of the major and minor axes respectively are shown as Major 1, 2, 3 and Minor 1, 2, 3. The dotted curve is that obtained for a tubular aperture of the same cross-sectional area as that of each of the elliptical apertures.

Fig. 10.



Cylindrical Apertures of Elliptical Cross-Section.

Axes of Ellipse.	I.	·213 cm. and ·127 cm.
do.	II.	·317 cm. and ·080 cm.
do.	III.	·506 cm. and ·051 cm.

As will be seen from fig. 10 in the elliptical cases, the eddies observed were not true sections of right circular vortex rings, for although the normal projection of the ring on to the diaphragm was a circle, yet the distance of the ring from the diaphragm was different along different longitudinal sections.

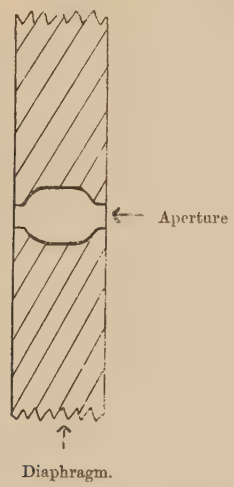
The fact that when the ratio of the axes of the ellipse was nearly equal to unity the phenomena were nearly those produced by two circles having for their diameters the axes of the ellipse, and yet as the axes ratio of the ellipse increased this was not the case, was due to the eddies being initiated at different critical velocities for different diameter apertures.

Part VI.

Non-Cylindrical Apertures.

These investigations were begun with the view of throwing light upon the flow of a gas through the stomata of plants. These stomata are usually non-cylindrical, as well as being elliptical in cross-section. In order to lead up to such cases, apertures with barrel-shaped cavities were constructed for the large observation chamber, and experiments were made with them. Fig. 11 shows a section of such an aperture.

Fig. 11.



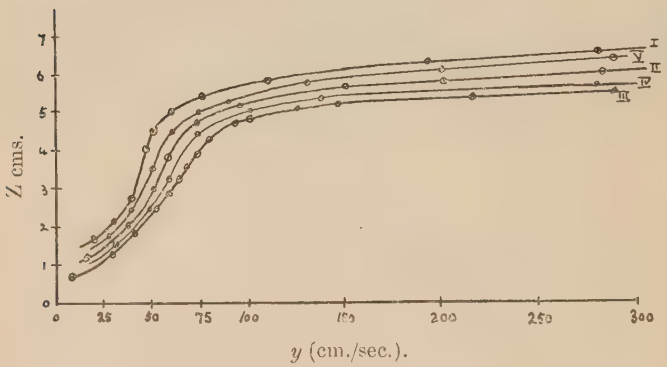
Section of Diaphragm.

Five apertures were made, each having the same diameter at both entrance and exit (=·159 cm.), and having different internal diameters varying from ·159 cm. to 1·27 cm. Each was in turn mounted in the chamber, and the longitudinal distances of the eddy centres measured for various mean velocities of the gas in the aperture.

Again, these two quantities were plotted on a graph (fig. 12). It was found that in no case were the eddy-centres further away from the diaphragm than in the case of a cylindrical aperture of circular cross-section, but varied with the amount of curvature of the section of the aperture. The eddy centres were nearest to the diaphragm when the internal diameter of the aperture was 3·3 times the external

diameter, and, when the diameter ratio was greater or less than this number, the eddy-centre distances approached that of the right circular case.

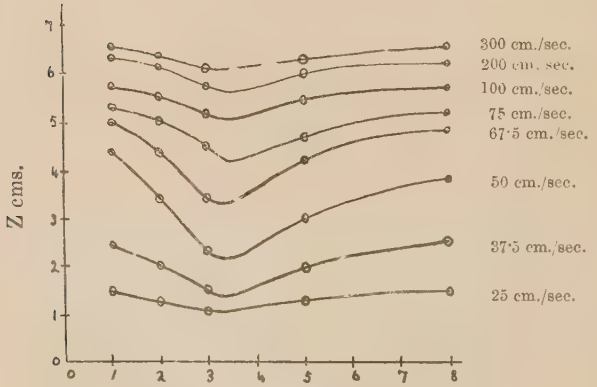
Fig. 12.



Non-Cylindrical Apertures.

Internal Diameter of Aperture :—I. ·159 cm. II. ·318 cm. III. ·477 cm. IV. ·795 cm. V. 1·27 cm.

Fig. 13.



This was shown very clearly by plotting the eddy-centre distances against the greatest internal diameter of the aperture for eight different mean velocities of the gas in the aperture (fig. 13).

LXX. *A New Determination of the Constant* N *of Avogadro.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I SHOULD like to call to your attention several errors, arithmetical and otherwise, which occur in the interesting paper by Dr. du Noüy, in the October issue of the Philosophical Magazine (Phil. Mag. No. 286, pp. 664–672, "A New Determination of the Constant N of Avogadro, based on its Definition").

1. He states on page 668 that his value $6{\cdot}003 \times 10^{23}$ agrees within 0·1 per cent. with the value found by Millikan ($6{\cdot}062 \times 10^{23}$). Of course this should be approximately 1·0 per cent.

2. He states on page 671 that his probable error is 0·15 per cent., and that therefore his value for N is

$$N = 6{\cdot}003 \pm 0{\cdot}08.$$

This should be

$$N = 6{\cdot}003 \pm 0{\cdot}009.$$

Apparently, his value and that of Millikan agree within the experimental error. Actually, they do not so agree.

3. Three so-called "control" calculations are made on pp. 668 and 669. He states "It is not unnecessary to remark that there is no fallacy whatever in the foregoing reasoning, etc." Elementary considerations show that the three experiments are dependent on one another and that the three "control" calculations are fallacious.

Let

A = surface of adsorption,

m = mass of liquid,

c_1, c_2, c_3 = concentrations of Sodium Oleate in the three minimum surface tension experiments,

ρ = density of Sodium Oleate,

w = molecular weight,

t_1, t_2, t_3 = three dimensions of the molecule,

V = volume of the molecule,

M = the mass of one molecule,

a = horizontal area occupied by a vertical molecule,

n = number of molecules present;

then

$$t_1=\frac{m}{\rho A}c_1,\quad t_2=\frac{m}{\rho A}c_2,\quad t_3=\frac{m}{\rho A}c_3,$$

$$V=t_1\,.\,t_2\,.\,t_3\;=\left(\frac{m}{\rho A}\right)^3 c_1\,.\,c_2\,.\,c_3,$$

$$M=\rho\left(\frac{m}{\rho A}\right)^3 c_1\,.\,c_2\,.\,c_3,$$

$$a=t_2\,.\,t_3,$$

$$n=\frac{mc_1}{M}=\frac{mc_1}{\rho\left(\frac{m}{\rho A}\right)^3 c_1\,.\,c_2\,.\,c_3},$$

$$na=\frac{\left(\frac{m}{\rho A}\right)^2 c_2\,.\,c_3\times mc_1}{\rho\left(\frac{m}{\rho A}\right)^3 c_1\,.\,c_2\,.\,c_3}=A.$$

Suppose

$$c_1\longrightarrow c_1+\triangle_1,$$
$$c_2\longrightarrow c_2+\triangle_2,$$
$$c_3\longrightarrow c_3+\triangle_3.$$

Then

$$na=\frac{\left(\frac{m}{\rho A}\right)^2 m(c_1+\triangle_1)(c_2+\triangle_2)(c_3+\triangle_3)}{\rho\left(\frac{m}{\rho A}\right)^3 (c_1+\triangle_1)(c_2+\triangle_2)(c_3+\triangle_3)}=A.$$

To check this, I assumed that the three minima occurred at the same concentration, 10^{-6}, then

$$t_1=t_2=t_3=\frac{mc_1}{\rho A}=9{\cdot}23\times10^{-8}\text{ cm.}$$

volume of molecule $=(9{\cdot}23)^2\times10^{-24}$

$=786{\cdot}3\times10^{-24}$ cu. cm.

mass of 1 molecule $=645{\cdot}55\times10^{-24}$ gram.

horizontal space occupied by one molecule

$=(9{\cdot}23)^2\times10^{-16}=85{\cdot}19\times10^{-16}$ sq. cm.

molecules in solution $=\dfrac{2\times10^{-6}\times10^{24}}{645{\cdot}55}=3{\cdot}1\times10^{15}$

$$A=3{\cdot}1\times10^{15}\times85{\cdot}19\times10^{-16}=26{\cdot}41\text{ sq. cm.}$$

This result is the same as the ones obtained in his control calculations.

Yours truly,

L. M. Alexander,
Asst. Prof. of Physics.

University of Cincinnati.
November 7, 1924.

LXXI. *On the Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour.* *By* Prof. J. R. Partington, *D.Sc.*, *and* M. F. Carroll, *M.Sc.**

Carbon Monoxide.

THE values of C_p, C_v, and γ for carbon monoxide recorded in the literature show little agreement. The earliest measurement is that of Delaroche and Berard †, who used the method of mixtures, and obtained the value $C_p = 8{\cdot}075$ cals. for the temperature range 15°–100° C. Dulong ‡ determined the velocity of sound in carbon monoxide by measuring the frequency of a reed blown by the gas, and comparison with a siren. He assumed the velocity of sound in air to be $V = 333$ m./sec., and the variation of velocity with temperature to be $V_t = V_0(1 + 0{\cdot}00375t)$, where V_t and V_0 are the velocities at $t°$ and 0° C. respectively. Dulong's values require correction for: (1) deviation from the gas laws, and (2) incorrect density values. The value assumed for V_0 in air is also too high: after correction, the value $\gamma = 1{\cdot}405$ at 15° C. is found.

Suermann § obtained by Delaroche and Berard's method a value for the dry gas, which on recalculation gives $\gamma = 1{\cdot}410$ at room-temperature.

Masson ‖ improved Dulong's method by using a sonometer wire instead of a siren, and found $V = 339{\cdot}76$ m./sec., which on recalculation gives the rather high value $\gamma = 1{\cdot}425$ at 15° C.

Regnault ¶ found directly $C_p = 6{\cdot}860$ cals., which gives $\gamma = 1{\cdot}409$ at room-temperature to 190°.

Cazin ** improved the Desormes and Clement method by the use of a larger vessel (60 litres), the tap being mechanically operated, and the time occupied in opening and closing the tap (about 0·03 sec.) recorded on a revolving band. He obtained for the diatomic gases N_2, H_2, O_2, CO, etc., the same value $\gamma = 1{\cdot}410$. These results require corrections

* Communicated by the Authors.

† *Ann. Chim. et Phys.* lxxxi. p. 98 (1812).

‡ *Ann. Chim. et Phys.* xli. p. 113 (1829).

§ *Ann. d. Physik*, xli. p. 474 (1837).

‖ *Ann. Chim. et Phys.* liii. p. 257 (1858); Phil. Mag. xiii. p. 523 (1857).

¶ *Mém. de l'Acad.* xxvi. p. 1 (1862).

** *Ann. Chim. et Phys.* lxvi. p. 706 (1862); Phil. Mag. xl. pp. 81, 197 (1870).

which cannot now be applied, since the constants of the apparatus are not known.

Wiedemann * improved Regnault's method by the substitution of tubes packed with metal turnings for Regnault's heating spiral. The carbon monoxide was prepared from potassium ferrocyanide and sulphuric acid, and probably contained small amounts of impurities, such as hydrocyanic acid vapour, which would tend to give a low result for γ. The value $C_p = 6{\cdot}793$ cals., which gives $\gamma = 1{\cdot}385$ at 15° C., was found.

Wüllner's † work was affected by the presence of impurities, since the experiments themselves are fairly accurate. He used the Kundt method and obtained for the velocity of sound in dry air the accurate value $V = 331{\cdot}90$ m./sec. at 0° C. When corrected from modern data, Wüllner's result $\gamma = 1{\cdot}403$ gives $\gamma = 1{\cdot}401$ for carbon monoxide.

Scheel and Heuse ‡ used an elaborate improvement of the Callender and Barnes constant-flow method. Their results with various gases agree fairly well with those obtained by other methods, although C_p is slightly high in most cases. They obtained for carbon monoxide $\gamma = 1{\cdot}398$ at 18° C.

Schweikert § employed a slight modification of Kundt's method, but used as the standard gas ordinary instead of dry air. He found $\gamma = 1{\cdot}407$, which on correction gives $\gamma = 1{\cdot}403$ at 0° C.

Hydrocyanic Acid.

The only previous measurement of the specific heat of hydrocyanic acid appears to be an approximate determination made by Usherwood ||, who used the Kundt method at various temperatures from 65° C. to 210° C. As the critical constants of the gas have not been determined, and therefore any equation of state involving their use cannot be applied to calculate the true value of γ obtained, Usherwood employed an empirical equation giving a correcting factor as a function of the observed density :—

$$PV = RT(1 + Pf_1(T) + P^2 f_2(T) + \ldots).$$

Terms after $Pf_1(T)$ were neglected, and Reech's Theorem then gives :

$$\gamma_{gas} = \gamma_{air} \frac{M_{gas}}{M_{air}} \left(\frac{\lambda/2 \text{ gas}}{\lambda/2 \text{ air}}\right)^2 (1+\alpha)^2,$$

* *Ann. d. Physik*, clvii. p. 1 (1876).
† *Ann. d. Physik*, clvii. p. 321 (1876).
‡ *Ann. d. Physik*, xxxvii. p. 79 (1912) ; xl. p. 473 (1913).
§ *Ann. d. Physik*, xlviii. p. 593 (1915) ; xlix. p. 433 (1916).
‖ J. C. S. (T.) cxxi. p. 1604 (1922).

where M = molecular weight, λ = wave-length of sound, and $(1+\alpha)$ is the ratio of the observed to the theoretical (ideal) density.

With the rough approximation $C_p - C_v = R = 2$ cals., the theoretical values of γ were calculated, and found to agree remarkably well when the assumptions made are considered. The values obtained by Usherwood are shown in Table VII. at the end of this paper, together with the corrected values. In the correction, the value of γ for air, assumed constant and equal to 1·403 over the range of temperature employed, is taken from 1·403 at 20° C. to 1·397 at 200° C. The use of narrow tubes, which, contrary to the statement of this author, has an appreciable effect on the velocity of sound, is difficult to allow for, since the diminution in velocity due to the radius is not even the same for different gases in the same tube, and in the case under consideration would be appreciable. The assumption $C_p - C_v = 2$ cals. for hydrocyanic acid is probably far from correct at the temperatures employed. This is shown in the case of certain vapours in the tables given by Partington and Shilling *, and especially for water, which bears a strong resemblance to hydrocyanic acid in some of its physical properties. The density factor $(1+\alpha)$ used is also open to criticism, since the experimental densities were apparently obtained on the assumption that the compressibilities of air and hydrocyanic acid are identical, whereas the correction for the deviation from the gas laws for the latter substance is larger than that for air. Vapour-densities determined by the Dumas method, however, can hardly be worth correction. The gas used, obtained by the action of dilute sulphuric acid on potassium cyanide, scarcely fulfils the purity requirements for the determination of physical constants, and there is no mention made of precautions taken to prevent contamination of the vapour by air, due to leakage into the apparatus. It will be obvious that the results obtained by Usherwood, although interesting and useful, can be regarded as approximate only.

Experimental.

The method used, a modification of that of Behn and Geiger, has been fully described in a previous paper †, and only the preparation of the gases will be treated in detail here. All other details of procedure were exactly as described in the reference given.

* 'Specific Heats of Gases,' p. 204 *et seq.* Benn Bros., Ltd. 1924.

† Partington and Shilling, Phil. Mag. xlv. p. 426 (1923).

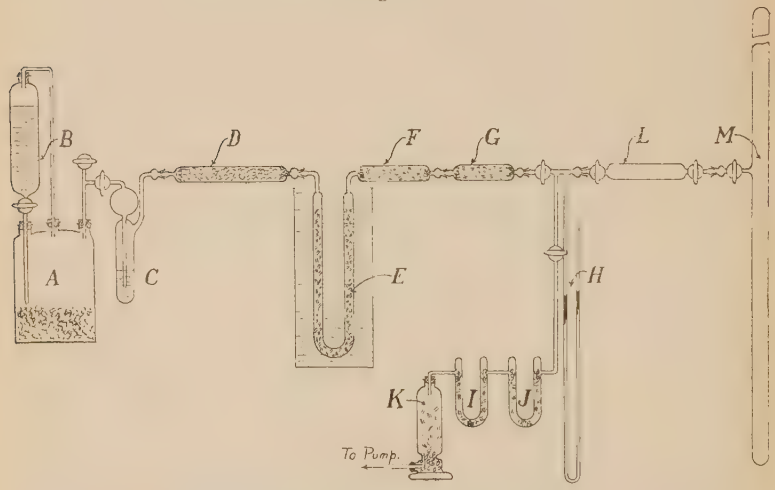
The tube correction factors for the tubes used in these experiments were found by experiment to be :—

Tube A	.....	Correction factor	= 1·0050
„ B	.....	„	= 1·0028
„ C	.....	„	= 1·0071

Preparation of Hydrocyanic Acid.

The apparatus is shown and described in fig. 1.

Fig. 1.



A is a three-necked bottle containing calcium sulphide, B a tap funnel containing dilute hydrochloric acid, C a water bubbler, D a calcium chloride tube, E a tube containing small crystals of mercuric cyanide, immersed in a water bath at 30° C.–40° C., F and G are phosphorus pentoxide tubes, H is a mercury manometer, J a phosphorus pentoxide tube, I a tube containing caustic potash sticks, K a caustic potash tower to absorb the gas, L a sample tube, and M the gas tube.

Pure hydrocyanic acid vapour produced by the reaction :

$$Hg(CN)_2 + H_2S = HgS + 2HCN,$$

passed through the drying tubes G and H which contained phosphorus pentoxide, and then through the sampler L to the gas-tube M. The completeness of the reaction was shown by the fact that while the salt in one limb of the tube E was completely blackened, the crystals in the other limb remained

quite white. As an extra precaution a piece of lead acetate paper was inserted in the tube F adjoining the glass joint, and remained unchanged. When the gas-tube had been filled the taps were closed, the tubes removed, and the gas in the sampler L treated with 5 per cent. caustic potash solution, which completely filled the tube. All the joints in the apparatus were of ground-glass, sealed on the outside, when necessary, with Faraday's cement. Before use, the apparatus was evacuated to 10 mm. and allowed to stand overnight; the pressure remained constant. When filling the apparatus any escape of poisonous gas was avoided: (*a*) in the case of carbon monoxide by bubbling through ammoniacal cuprous chloride solution; (*b*) in the case of hydrocyanic acid by leading the vapour through caustic soda solution, and then through the water-pump, the end of which led into the open air.

Results for Hydrocyanic Acid.

The gas-tube was filled as previously described. Measurements were made as in previous experiments, the temperature and pressure being so adjusted that the vapour was well above the point of liquefaction, and the mean value of γ' determined.

The chief difficulty in calculating γ from γ' is the choice of the correction factor. Although the critical constants for hydrocyanic acid are not known, they can be calculated to some degree of approximation for use in a correction term by methods due to P. Walden *, together with some other empirical relations.

Walden finds the following relation:

$$P_c = K_1 T_s / V_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_c is the critical pressure, V_s the molecular volume at the boiling-point T_s, and K_1 is a constant. Again,

$$D_c / D_s = K_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where D_c and D_s are the densities of the liquid at the critical point and boiling-point respectively, and K_2 is a constant. These, together with the well-known relations †:

$$P_c V_c / T_c = K_3,$$

and

$$T_c / T_s = K_4,$$

give values for T_c and P_c.

* *Zeit. phys. Chem.* lxvi. p. 385 (1909).

† Guldberg, *Zeit. phys. Chem.* v. p. 374 (1890).

With an approximate value of T_c we can calculate P_c, or *vice versa*, from van der Waals' vapour-pressure equation :

$$\log P_c/p = f(T_c/T-1), \quad . \quad . \quad . \quad . \quad (3)$$

where f is a constant depending on the nature of the substance. The following values for the constants were calculated for normal and abnormal substances. The former are the values given by Walden, and the latter are those for substances which resemble hydrocyanic acid in certain physical properties, *e. g.* are strongly ionizing media and possess a high dielectric constant :—

	K_1.	K_2.	K_3.	K_4.	f.
Normal substances.....	12·45	2·45	21·8	1·55	3·10
Abnormal substances.....	11·35	2·89	18·9	1·695	2·80

Using the data for abnormal substances, with $D_s = 0·690$, we find for hydrocyanic acid,

from (1), $P_c = 87$ atmos. ; from (2), $P_c = 83·7$ atmos. ;

from (3), $P_c = 87·1$ atmos.,

giving a mean of

$$P_c = 85 \text{ atmos. approx.},$$

and hence

$$T_c = 506° \text{ abs.}$$

Using the data for normal substances, we find similarly :

$$P_c = 52 \text{ atmos.}, \quad \text{and} \quad T_c = 464° \text{ abs.}$$

The values of P_c may be compared with the values for normal and abnormal substances of low molecular weight :

Normal.

Substance.....	Air.	N_2.	O_2.	C_2H_2.	CH_4.	C_2H_4.	C_2H_6.
P_c atm.	= 39·3	33	50·2	68	45·6	50·2	51

Abnormal.

Substance.....	HCl.	SO_2.	NO_2.	NH_3.	H_2O.
P_c atm.	= 82·4	78·9	100	115	217

The *abnormal values* when substituted in the correction term give :

$$\phi = 1·0265 \text{ at } 422 \text{ mm. and } 21°·0 \text{ C.} \quad . \quad . \quad (4)$$

The *normal values* give :

$$\phi = 1·0334 \text{ at } 422 \text{ mm. and } 21°·0 \text{ C.} \quad . \quad . \quad (5)$$

It will be observed that with either correction factor there is fair agreement; thus, with the value $\gamma' = 1{\cdot}2438$, we find from (4) $\gamma = \gamma'\phi = 1{\cdot}275$, and from (5) $\gamma = \gamma'\phi = 1{\cdot}281$. We have adopted the value of ϕ deduced from the *normal* constants, for the reasons given in a later section. A typical specimen of the results is Table I., and Tables II. and III. contain the mean values for the two series of experiments at different temperatures and pressures.

TABLE I.

Hydrocyanic Acid.

Exp. (1). Pressure = 422 mm. T = 21°·0 C.

Tube A. Correction factor = 1·0050.

Air Tube.					Gas Tube.				
No.	A.	B.	Mean.	λ/2 cm.	No.	A.	B.	Mean.	λ/2 cm.
14.	90·6	90·1	90·60	6·471					
	91·0	90·5							
13.	84·5	84·4	84·40	6·492	13.	82·6	82·0	82·20	6·323
	84·2	84·4				82·4	82·4		
12.	77·9	77·8	77·83	6·485	12.	75·7	75·8	75·75	6·313
	77·9	77·7				75·7	75·8		
11.	71·3	71·3	71·25	6·477	11.	69·3	69·0	69·40	6·309
	71·2	71·2				70·0	69·3		
10.	64·9	65·1	64·83	6·483	10	62·7	62·2	63·10	6·310
	64·7	64·6				63·7	63·8		
9.	58·5	58·3	58·35	6·483	9.	56·5	56·6	56·79	6·303
	58·2	58·4				56·9	56·9		
8.	52·2	51·8	51·83	6·478	8.	50·7	50·8	50·63	6·328
	52·2	51·8				50·8	50·2		
7.	45·4	45·5	45·35	6·479	7.	44·1	43·7	44·18	6·311
	45·3	45·2				44·7	44·0		
6.	39·3	38·9	38·90	6·483					
	38·7	38·7							
		Mean		6·482			Mean		6.314

λ/2 for gas corr. = 6·314 × 1·0050 = 6·334 cm.

TABLE II.

Hydrocyanic Acid.

Pressure = 422 mm.

Tube A. No. of exp.	λ/2 Dry air. cm.	λ/2 HCN. cm.	λ/2 HCN corr. cm.	γ'.	$t°$ C.
(1)	6·482	6·303	6·334	1·247	21·0
(2)	6·502	6·314	6·346	1·246	21·3
(3)	6·494	6·297	6·329	1·243	21·1
(4)	6·511	6·311	6·343	1·241	21·4
(5)	6·484	6·308	6·339	1·248	21·2
(6)	6·491	6·320	6·352	1·249	21·2
(7)	6·518	6·339	6·371	1·249	21·8
(8)	6·515	6·319	6·351	1·243	21·8
(9)	6·538	6·343	6·375	1·244	22·2
(10)	6·537	6·351	6·384	1·247	22·2
Tube C.					
(1)	7·026	6·782	6·839	1·240	20·0
(2)	7·038	6·811	6·858	1·241	20·0
(3)	6·949	6·725	6·772	1·242	19·7
(4)	6·965	6·735	6·781	1·244	19·7
(5)	7·057	6·826	6·873	1·243	20·2
(6)	7·038	6·813	6·860	1·244	20·2
(7)	7·038	6·802	6·847	1·238	20·2
(8)	7·088	6·824	6·873	1·240	20·2

Mean ..... $\gamma' = 1{\cdot}2438$ at 20°·80 C.

TABLE III.

Hydrocyanic Acid.

Pressure = 505 mm.

Tube A. No. of exp.	λ/2 Dry air. cm.	λ/2 HCN. cm.	λ/2 HCN corr. cm.	γ'.	$t°$ C.
(1)	6·473	6·197	6·229	1·211	17·1
(2)	6·484	6·205	6·236	1·209	17·3
(3)	6·484	6·229	6·261	1·218	17·5
(4)	6·486	6·238	6·270	1·222	17·5
(5)	6·479	6·211	6·243	1·215	17·1
(6)	6·469	6·210	6·241	1·217	17·1
(7)	6·486	6·208	6·246	1·212	17·5
(8)	6·487	6·214	6·240	1·212	17·5

Mean ..... $\gamma' = 1{\cdot}2145$ at 17°·35 C.

The second series of experiments shows the necessity for keeping the temperature and pressure constant during the experiments. A difference of pressure of 20 mm., or a difference of temperature of 1° C., affects the results to the extent of five units in the third place of decimals, which, in the case of hydrocyanic acid near the point of liquefaction, is greater than the experimental error. A slight decrease of temperature or increase of pressure causes the value of γ to fall rapidly, whereas for "permanent" gases a large increase of pressure causes a comparatively small increase of γ. It is probable that at the second temperature and pressure 17°·35 C. and 505 mm., the vapour of hydrocyanic acid is near its point of liquefaction. Corresponding with the *normal* value of $\phi = 1{\cdot}0334$, we find :

$$C_p - C_v = R\phi' = 1{\cdot}9875 \times 1{\cdot}0713$$
$$= 2{\cdot}130 \text{ cals. at } 422 \text{ mm. and } 20°{\cdot}8 \text{ C.},$$

and similarly, for $\phi = 1{\cdot}04024$, we find :

$$C_p - C_v = R\phi' = 1{\cdot}9875 \times 1{\cdot}0880$$
$$= 2{\cdot}160 \text{ cals. at } 505 \text{ mm. and } 17°{\cdot}35 \text{ C.}$$

Hence at 20°·8 C. and 422 mm. :

$$\gamma = 1{\cdot}281, \quad C_p = 9{\cdot}69 \text{ cals.}, \quad C_v = 7{\cdot}56 \text{ cals.},$$

and at 17°·35 C. and 505 mm. :

$$\gamma = 1{\cdot}268, \quad C_p = 10{\cdot}22 \text{ cals.}, \quad C_v = 8{\cdot}06 \text{ cals.}$$

for hydrocyanic acid vapour.

Preparation of Carbon Monoxide.

The gas was prepared by the action of pure concentrated sulphuric acid on sodium formate in the cold, and purified by passing through concentrated sulphuric acid, over caustic potash sticks, and over phosphorus pentoxide.

The apparatus was similar to that used for the preparation of hydrocyanic acid, except that tubes containing caustic potash sticks were substituted for the mercuric cyanide tube. The tap tube L was used to sample the gas, which was analysed by absorbing the carbon monoxide in ammoniacal cuprous chloride solution, and any residual gas estimated as air if in sufficient quantity. With the exception of two experiments the gas was completely absorbed, and in the former cases it was shown to contain 0·7 per cent. and

0·3 per cent. of air, respectively. Calculation of C_v shows that these amounts will not affect γ by more than 0·001, *i. e.* about the limit of the experimental error.

Results for Carbon Monoxide.

The tube was filled with the gas and a series of experiments made. It was then refilled and another series taken. When refilling, the tube was only evacuated once or twice, since it was already full of the pure gas. The results were tabulated and the mean value of $\lambda/2$ for the gas tube was then corrected by multiplying by the previously determined tube correction factor for that particular tube; γ' was then calculated from the equation:

$$\gamma'_{\text{gas}} = \gamma'_{\text{air}} \times \left(\frac{M_{\text{gas}}}{M_{\text{air}}}\right) \times \left(\frac{\lambda/2 \text{ gas}}{\lambda/2 \text{ air}}\right)^2.$$

TABLE IV.

Carbon Monoxide.

Exp. (3). $t = 11°{\cdot}5$ C.

Tube A. Correction factor = 1·0050.

Air Tube.					Gas Tube.				
No.	A.	B.	Mean.	$\lambda/2$ cm.	No.	A.	B.	Mean.	$\lambda/2$ cm.
12.	81·3	81·9	81·53	6·794	12.	82·1	82·7	82·48	6·873
	81·2	81·7				82·4	82·7		
11.	74·3	74·6	74·69	6·782	11.	75·7	75·9	75·60	6·872
	74·4	74·9				75·3	75·5		
10.	67·9	67·9	67·80	6·780	10.	68·5	68·3	68·50	6·850
	67·7	67·7				68·5	68·7		
9.	61·0	61·0	61·05	6·783	9.	62·0	62·3	61·93	6·881
	61·1	61·1				61·7	61·7		
8.	54·2	54·3	54·25	6·781	8.	54·9	54·7	54·73	6·847
	54·5	54·0				54·7	54·8		
7.	47·5	47·7	47·53	6·789	7.	48·5	47·9	48·30	6·886
	47·3	47·6				48·6	48·4		
6.	40·7	40·8	40·70	6·783	6.	41·3	41·1	41·20	6·867
	40·6	4·05				41·2	41·2		
			Mean =	6·785				Mean =	6·869

$\lambda/2$ for gas corr. = 6·869 × 1·0050 = 6·904 cm.

The mean of the experimental values was corrected for deviations from the ideal gas state by Berthelot's equation :

$$\gamma = \gamma'\phi = \gamma'[1 - \tfrac{9}{64}\pi\tau(1 - 6\tau^2)],$$

where

$$\pi = P/P_c \quad \text{and} \quad \tau = 1/\theta = T_c/T,$$

and C_p and C_v were then calculated by means of the equation :

$$C_p - C_v = R\phi',$$

where

$$R = 1{\cdot}9875 \text{ cals.} \quad \text{and} \quad \phi' = (1 + \tfrac{27}{16}\pi\tau^3).$$

A typical series is shown in Table IV., and the final results are tabulated in Table V.

TABLE V.

Carbon Monoxide.

Pressure = 760 mm.

Tube A.

No. of exp.	λ/2 Dry air. cm.	λ/2 CO. cm.	λ/2 CO corr. cm.	γ'.	$t°$ C.
(1)	6·779	6·853	6·888	1·403	11·1
(2)	6·784	6·848	6·884	1·400	11·1
(3)	6·785	6·869	6·904	1·403	11·5
(4)	6·778	6·856	6·893	1·402	10·3
(5)	6·776	6·859	6·893	1·405	10·3
Tube B.					
(1)	6·679	6·777	6·795	1·404	9·9
(2)	6·679	6·780	6·798	1·405	9·9
(3)	6·670	6·774	6·793	1·407	9·8
(4)	6·688	6·778	6·795	1·401	10·5
(5)	6·674	6·772	6·789	1·404	9·9
(6)	6·685	6·782	6·801	1·404	10·1
(7)	6·682	6·779	6·797	1·403	10·1

Mean ..... $\gamma' = 1{\cdot}4035$ at 10°·3 C.

From the mean values obtained for γ' and t, and the most recent critical data for carbon monoxide *, $P_c = 34{\cdot}6$ atmos., $T_c = 134°{\cdot}4$ abs., we find :

$$\phi = 1{\cdot}000675 \quad \text{and} \quad \phi' = 1{\cdot}0053,$$

whence

$$C_p - C_v = 1{\cdot}998 \text{ cals.}$$

* Cardoso, *J. Chim. Phys.* xiii. p. 312 (1915).

Thence for carbon monoxide at 10°·3 C.:

$\gamma = 1{\cdot}404$; $C_p = 6{\cdot}940$ cals.; and $C_v = 4{\cdot}942$ cals.

As the values of C_v are practically constant over a small range of temperature, a comparison of the specific heats of permanent gases is rendered fairly simple. The close agreement of the values (all found in this laboratory) of γ, C_p, and C_v for nitrogen and carbon monoxide is shown in Table VI. Nitric oxide, a similar gas in some respects, is also included.

TABLE VI.

Specific Heats of Nitrogen, Carbon Monoxide, and Nitric Oxide.

Gas.	t° C.	M.	N.	γ.	C_p.	C_v.
N_2	16·7	28	10	1·405	6·93	4·93
CO	10·3	28	10	1·404	6·94	4·94
NO	7·6	30	11	1·400	7·00	5·00

N is the number of electrons in the outer shell of the molecule according to the Lewis-Langmuir theory. Results with nitrous oxide and carbon dioxide over a range of temperatures * show that such agreement is purely accidental, and the specific heat is not the same when the molecular weights and hypothetical external electronic structures are identical.

Discussion of the Results obtained for Hydrocyanic Acid.

The question of the applicability of Berthelot's equation of state to associated vapours and the method used in calculating the critical constants may be briefly discussed. Berthelot's equation has been extensively used for the calculation of the specific heats from values of γ' obtained by the velocity of sound and the adiabatic expansion methods, and gives good agreement in both cases when permanent gases are used. In the case of steam, Callendar's empirical equation of state is almost certainly more reliable, but it is not known whether it can be used for other associated vapours. The application of Callendar's equation to the calculation of γ from the experimental values of C_p or C_v leads

* Partington and Shilling, unpublished.

to results which differ appreciably from those obtained by the use of Berthelot's equation, especially near the boiling-point, as is shown by the following figures for steam * :—

At 100° C.	Callendar's equation	gives	$\gamma = 1{\cdot}330$
„ „	Berthelot's „	„	$\gamma = 1{\cdot}310$
„ 200° C.	Callendar's „	„	$\gamma = 1{\cdot}312$
„ „	Berthelot's „	„	$\gamma = 1{\cdot}307$

The correction terms deduced from Berthelot's equation and Usherwood's density correction show much greater discrepancies. This is shown in Table VII., together with the experimental results obtained. The actual experimental results for γ' were not given in the paper, but have been calculated by dividing γ by the correcting term $(1+\alpha)^2$.

Table VII.

$t°$ C.	ϕ.	$(1+\alpha)^2$.	γ_1.	γ_2.	γ_3.	γ_4.	γ_5.
65	1·0367	1·077	1·214	1·212	1·310	1·308	1·256
100	1·0278	1·041	1·245	1·242	1·296	1·293	1·277
140	1·0199	1·010	1·266	1·262	1·277	1·275	1·288
182	1·0176	1·002	1·248	1·243	1·248	1·243	1·263
210	1·0145	1·001	1·238	1·231	1·238	1·241	1·250

In this table : ϕ = Berthelot's correcting term, assuming the values $P_c = 52$ atmos. and $T_c = 464°$ abs.; $(1+\alpha)^2$ = Usherwood's correcting term ; γ_1 = Usherwood's experimental γ' values : γ_2 = Usherwood's experimental values corrected for variation of γ for air with temperature ; γ_3 = Usherwood's experimental values using the correcting term $(1+\alpha)^2$, assuming γ for air = 1·403 (constant) ; γ_4 = Usherwood's experimental values using this correcting term, but corrected for variation of γ for air with temperature ; γ_5 = Usherwood's experimental values using Berthelot's correcting term and correcting for variation of γ for air.

These results are also represented on the graphs in fig. 2.

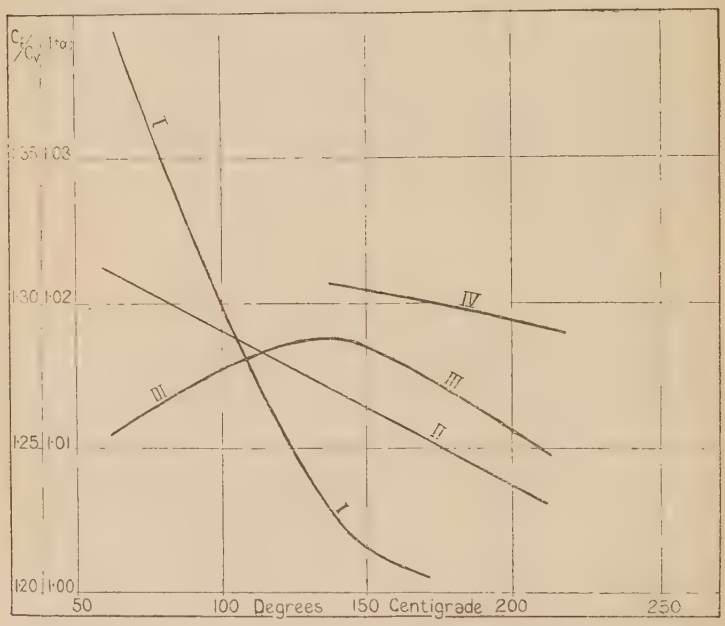
Curve I. represents the value of $(1+\alpha)$ obtained from

* Partington and Shilling, 'The Specific Heats of Gases,' p. 205.

Usherwood's density results. Curve II. gives the value of γ_4 at different temperatures. Curve III. gives the values of γ_5. Curve IV. gives the value of γ for carbon dioxide at corresponding temperatures.

It will be seen from the above that these results are open to different interpretations, and the factors affecting the results are far more complicated than has previously been supposed.

Fig. 2.



That association accounts for both Usherwood's and the present authors' results appears probable from the following considerations. As we approach the point of liquefaction the greater extent of the association is shown by Curve I., hence the greater are the apparent values of C_p and C_v, since these quantities must be greater for the associated molecules, and consequently the smaller is the value of γ. Thus, Curve III. shows that when the degree of association has become very small the value of γ reaches a maximum, and then decreases in an almost normal manner, as is shown by comparison with Curve IV. for a normal gas (carbon dioxide) at corresponding temperatures. This argument is confirmed by the present results, which show that γ decreases with increase of pressure and decrease of temperature near the point of liquefaction. It will thus be seen that owing to the

almost certain existence of association in the gaseous state, a determination of the specific heat of hydrocyanic acid does not necessarily afford any evidence of the existence of tautomerism. The assumption that a change of specific heat with temperature, as such, is to be interpreted as indicating the existence of tautomeric change is, of course, devoid of foundation. A similar difficulty is met with in the attempted determination of the specific heats of nitrogen dioxide, which associates according to the equation :

$$2NO_2 = N_2O_4.$$

This case has been investigated fairly completely, both from the experimental and theoretical standpoint, but even in this comparatively simple case there are many difficulties to be overcome, and the results are far from satisfactory *.

The choice of the correction term ϕ for hydrocyanic acid used by the present authors has yet to be justified. Even if the critical constants for hydrocyanic acid had been experimentally determined, their use in this correcting term would introduce difficulties for the following reasons. From the density measurements the degree of association can be obtained approximately from the equation :

$$\alpha = (D-d)/d,$$

where D is the theoretical density of $(HCN)_2$, d is the observed density of the mixture, and α is the degree of association of the compound $(HCN)_2=2HCN$. The equilibrium constant is given by :

$$K = \alpha^2 P/(1-\alpha),$$

and the heat of association, Q, can then be calculated from the equation :

$$\log K = -Q/RT+c,$$

where c is the constant of integration.

Thus, with sufficient data we can find the value of α at any temperature on the assumption that the heat of association is constant over the range employed. Using the density data of Usherwood we calculate, *at the critical point itself*, that α is very small, and therefore the vapour should consist almost entirely of double molecules. Therefore the values of the critical constants experimentally obtained should be mainly those of the substance $(HCN)_2$, which, from the physical point of view, is an entirely different substance from that used in the experiments ; or at least they are those of the simple and double molecules in equilibrium.

The authors have therefore made use of the correction

* Partington and Shilling, 'Specific Heats of Gases,' p. 188.

term deduced from the *normal values* of the physical constants of hydrocyanic acid, since, although the vapour is probably associated, the association is small. The association can be approximately estimated by means of the above equations, and was found to be between 5 and 10 per cent. at 20° C. and 422 mm., and between 8 and 13 per cent. at 17°·35 C. and 505 mm. In view of these considerations, the use of the experimental critical constants in the correction terms for associated vapours, such as steam and nitrogen dioxide, must be provisional, since these critical constants, as determined, are merely values for a mixture of the associated and unassociated molecules, and therefore cannot be applied to a mixture under different conditions, which is, in general, of a different composition.

Whereas the authors' experimental results are considered to be reasonably accurate, the values of γ, C_p, and C_v for hydrocyanic acid deduced from any equation of state must be only approximate, and all values will be "apparent" owing to the effect of such factors as heat of association. The disentanglement of so many complicated factors presents a problem which, although theoretically attractive, is distinctly formidable from the point of view of experimental investigation.

Summary.

The specific heats of carbon monoxide and hydrocyanic acid have been determined by a method depending upon the relative velocities of sound in these gases and in air.

The expected values for the specific heats of carbon monoxide have been confirmed, and some provisional values have been obtained for the ratio of the specific heats of hydrocyanic acid.

Table IX.

Gas.	t° C.	P mm. Hg.	$\gamma=C_p/C_v$.	C_p.	C_v.
Carbon monoxide	10·3	760	1·404	6·94 cals.	4·94 cals.
Hydrocyanic acid	20·8	422	1·282	9·69 „	7·56 „
„ „	17·35	505	1·268	10·22 „	8·08 „

The authors are indebted to Mr. W. G. Shilling, M.Sc., for valuable assistance and advice. One of them (M. F. C.) also wishes to thank the London County Council and the Chemical Society for grants which enabled him to carry out the work. The results form part of a Thesis presented to the University of London for the Degree of M.Sc. by M. F. Carroll.

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LXXII. *The Rectification of Alternating Currents by Crystals.* By Alfred Clive James *.

NO satisfactory explanation has yet been proposed of the property of some crystals of rectifying an alternating current, first discovered by Dunwoody in 1906 †.

Pierce (1907) suggested that the unilateral conductivity of carborundum was due to the small area of contact permitting the passage of electrons more readily in one direction than in the other.

In 1910, Eccles ‡ formulated a purely thermal theory of rectification, based on the Joule effect producing variations in the resistance of oxides and sulphides having large negative resistance coefficients. In 1913 § he deduced a very complete theory from electrothermal considerations. Neither of these theories is satisfactory.

The present attitude is that rectification is due to unilateral conductivity, so that when an alternating voltage is applied, the resulting mean current is a function of the alternating voltage ‖. Up to the present no satisfactory explanation of this unilateral conductivity has been proposed.

J. Strachan ¶ has recently proposed the theory that the loose contact acts as a metallic conductor in one direction and as a dielectric in the other. This seems probable. He then puts forward the hypothesis that the molecules have axes of conductivity, polar in nature and reversible. At the loose contact, changes of polarity, accompanied by actual movements of the molecules, take place. The definite orientation of the surface molecules as determined by crystal structure would result in definite orientation of the conductivity axes, yielding predominant properties in one direction and requiring greater expenditure of electrical energy, in the case of the current in the opposite direction, to reverse the conductivity axes. One pulse of the oscillation passes readily in the predominant direction of conductivity, but the other pulse is met by the dielectric conditions produced by the reluctance of the molecular movements to coincide with the tendency of reversal of the conductivity axes. There

* Communicated by the Author.
† U.S.A. Pat. Spec. 837616 (1906); Brit. Pat. Spec. 5332 (1907).
‡ Eccles, Proc. Phys. Soc. xxii. pp. 269 and 360 (1910).
§ Eccles, Proc. Phys. Soc. xxv. p. 273 (1913).
‖ D. W. Dye, Dict. of Applied Physics, ii. p. 647 (1922).
¶ Strachan, 'Wireless World,' xiv. p. 245 (1924).

seems to be little evidence upon which to base such a theory.

Electrolytic theories were early applied to explain crystal rectification, but so far very little experimental evidence has been produced to support them. In this paper, evidence is brought forward in support of a modification and extension of the old electrolytic theory.

The effect of silver sulphide in increasing the rectifying properties of galena seemed to require investigation. It was also noticed that in addition to possessing unilateral conductivity, on passing a current through a crystal of galena, one contact being a sharp point, the current was not constant. When the point was negative the current invariably rose. When the point was positive the behaviour was less certain. This will be discussed in detail later.

All the crystals used were synthetic, and were prepared by heating precipitated lead sulphide, with or without the addition of other sulphides, with a little sulphur to prevent oxidation, in an electric furnace to 1150° C. and allowing to cool very slowly. The crystals containing stannous sulphide had to be heated to 1250° C.

The Transition Point of Lead Sulphide.

A series of experiments was first carried out in order to find the effect of temperature on the unilateral conductivity of lead sulphide. The crystal was mounted in a brass cup and immersed in pure B.P. paraffin in a large test-tube, this tube also being placed in a bath containing B.P. paraffin. The paraffin immersion ensured the whole crystal being at the same temperature, and also kept the contact clean and free from oxidation. The most satisfactory contact was found to be a fine steel needle fused into a glass tube, connexion being made by mercury in the tube. The glass tube carrying the needle slid easily inside a wider tube, and the pressure of the point on the crystal was constant and approximately equal to the weight of the needle and the tube into which it was fused. A thermometer was also placed in the inner tube.

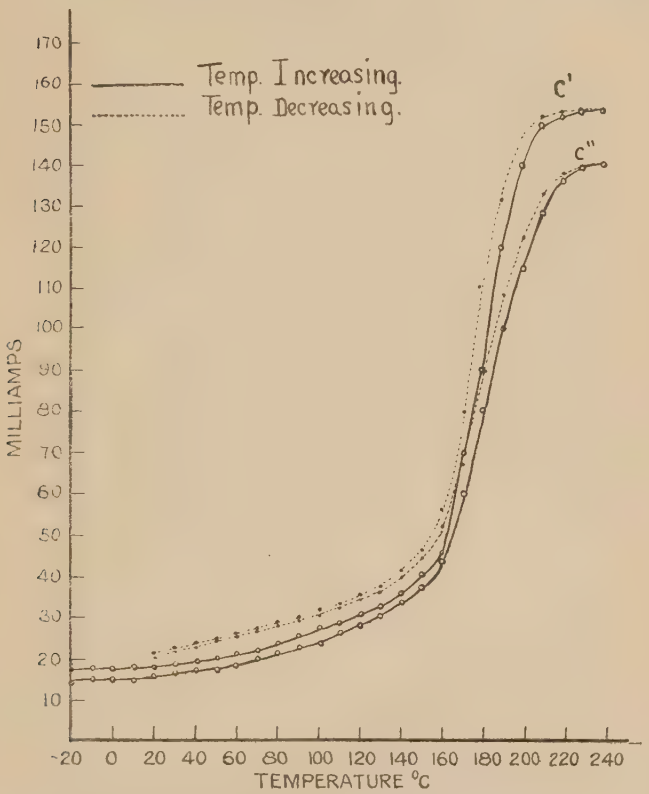
The crystal was connected in series with a commutator, a milliammeter, and a two-volt accumulator.

On making the circuit, the current passing through the crystal was not constant (*cf.* above). For this reason the current had to be read on the ammeter immediately on completing the circuit, and the current again broken.

The initial values of the current in each direction were

plotted against the temperature. The curve is shown in fig. 1. C′ is the current when the metallic point is negative, and C″ when positive. C″ was read first, then C′. It was found that the conductivity rose rapidly at 160° C., indicating that galena has a transition point at this temperature. Similar curves were obtained on cooling, but the conductivity

Fig. 1.



Temperature–Conductivity Curve for Lead Sulphide.

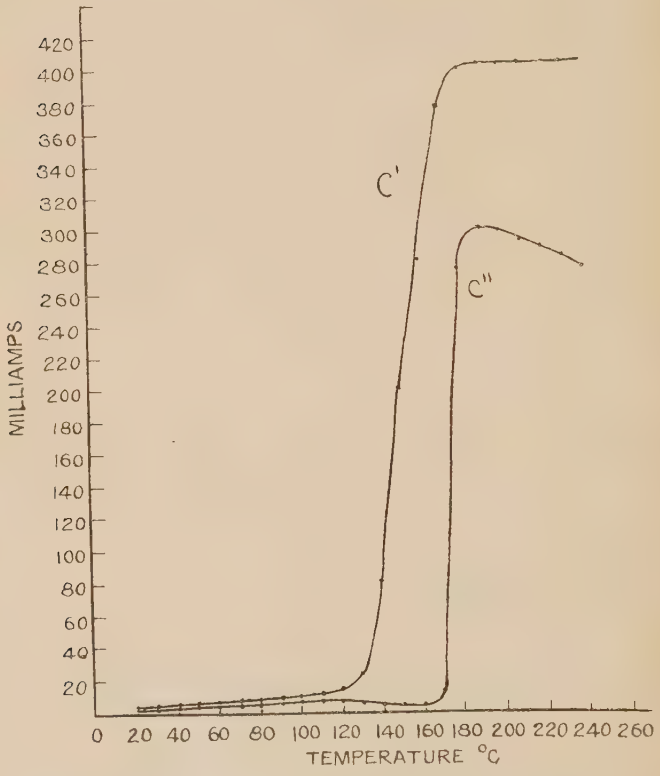
never fell to quite its original value. Streintz * (1904) also noticed that on heating a crystal of galena and then cooling, the conductivity was higher than originally. This is probably due to the α-form, stable above 160°, being present in a metastable state.

A similar curve was obtained for a crystal consisting

* F. Streintz, *Boltzmann-Festschrift* (1904).

of 90 per cent. lead sulphide and 10 per cent. silver sulphide, but it was found that the increase of conductivity at the transition point was more than trebled. The transition point had been lowered to 133° C. Thus, in the case of pure lead sulphide, the current increased from 45 to 150 milliamps, while in the case of the crystal containing 10 per cent. of silver sulphide it increased from 25 to 400 milliamps. (In this case curve C′ was read before C″) (fig. 2).

Fig. 2.



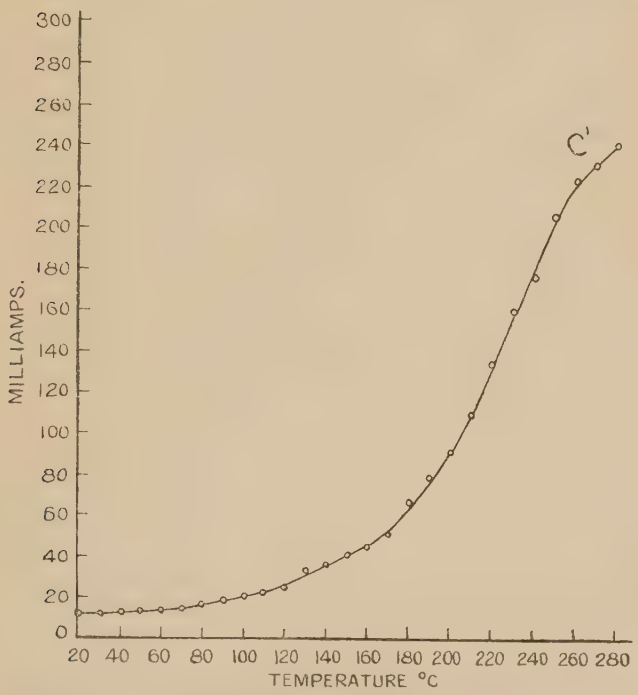
Temperature–Conductivity curves for Lead Sulphide+10 per cent. Silver Sulphide.

This transition point, at which there is a large increase of conductivity, is similar, but to a less extent, to that which occurs in silver iodide *. At 144°·6 C. the specific conductivity of silver iodide increases from $3{\cdot}4 \times 10^{-4}$ to 1·31.

* Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

A curve was also obtained for a crystal of 95 per cent. lead sulphide and 5 per cent. stannous sulphide. In this case the conductivities in the opposite directions were so nearly equal that only C′ was plotted (fig. 3). With lead sulphide the curve had become nearly horizontal at 210°, with lead sulphide containing 10 per cent. silver sulphide at 180°; but with lead sulphide containing 5 per cent. of stannous sulphide the current was still rising at 270°, the limit to which the paraffin bath could be taken with safety.

Fig. 3.



Temperature-Conductivity curve for Lead Sulphide+5 per cent. Stannous Sulphide.

This transition point of lead sulphide explains why crystals used for rectifying purposes are most sensitive when cooled very slowly. The usual explanation given is that with slow cooling the sulphide crystallizes better and well-defined crystals are obtained. It has been noticed in connexion with this work that crystals with a granular structure

are more satisfactory than those with well-defined faces. A more probable explanation is that unless the crystal is cooled slowly the α-form, stable above 160°, is present in a metastable state.

The Variation of Conductivity with Time.

It has already been mentioned that when a current is passed through a crystal of lead sulphide, one contact being a sharp point, the current is not constant, but if the point is negative, which is the low-resistance direction, rises steadily. The rate of increase decreases with time, and finally the current becomes constant. If the current is allowed to rise for a short time and is then reversed, the current has an initial value approximately equal to that before reversal, and then falls rapidly to the original value in that direction. The rise of the current is always fairly steady, but the fall is often erratic. The current may decrease slowly for a short time, and then fall instantaneously to the initial value.

The rise of current always occurs when the point is the cathode, and this suggests that the phenomenon is of an electrolytic nature. This suggestion is strengthened by the fact that the addition of silver sulphide to the crystal increases the rate and amount of this rise. Silver sulphide is known to conduct 80 per cent. of the current electrolytically below 179°, while above this transition temperature the conduction is wholly electrolytic *. If the current is carried electrolytically, it should be possible to detect a difference in weight of the electrode. A silver point weighting 0·03 gm. was used as electrode. It slid easily into a hole drilled in the end of a short piece of brass rod, and was pressed down on the crystal by means of an adjustable spring. The electrode was weighed by means of the torsion type of micro-balance. It was used both as anode and cathode, and crystals of pure lead sulphide and lead sulphide containing 10 per cent. of silver sulphide were used; but even after passing 50 milliamps for 24 hours, the weight of the electrode was constant to within 0·00003 gm., which is within the limits of experimental error. Hence it was concluded that electrolysis, at least of the ordinary type, could not occur. The suggestion arose, however, that the rise of current could be explained by the metal, instead of being deposited on the electrodes, forming metallic threads through the crystal.

* Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

Le Blanc and Kerschbaum * have stated that silver sulphide appears to conduct metallically because of the formation of fine threads of silver. The supposed metallic conduction of fused silver halides is also due to threads of silver stretching from pole to pole.

In 1898, Bernfeld † stated that the conductivity of lead sulphide increased with temperature. He also pressed lead sulphide between two silver plates and passed a current of one ampere for 20 hours. He found no alteration in the weight of his electrodes. This is similar to the results obtained above for small currents, and is also due to the formation of metallic threads which then conduct metallically. Guinchant ‡ and Aubel § (1903) stated that the conductivity decreased with rise of temperature. The differences in these results are probably due to metallic threads forming in Guinchant and Aubel's experiments, the conductivity of these threads decreasing with rise of temperature. Koenisberger ‖ (1909) considered that the conduction was metallic. The results given in this paper show that if the currents are momentary, metallic threads have not time to form, and the conductivity then rises with increase of temperature, due to a fraction of the current being conducted electrolytically.

It was found that, although the reversal of the current after it had been passing for a short time was accompanied by a decrease of the current due to the destruction of the metallic threads, if the current in the low-resistance direction was continued until it had become constant, it was found that on reversal, the current in the opposite direction was equal to, or even slightly higher than, that before reversal, and it did not fall. The explanation of this is that after a short time the threads are only formed for a short distance through the crystal, and on reversal the thread becomes the anode and is dissolved ; but that when the current has become constant the threads are formed right through the crystal, and the conduction is entirely metallic. The fact that when the current had become constant, the reverse current had a higher initial value than before reversal, is probably due to back E.M.F. No back E.M.F. of polarization could be observed after passing the current for a short time ; but this would be due to the fact that, the threads being short, the circuit would be completed through the crystal; but when the threads

* Le Blanc & Kerschbaum, *Zeit. Electrochem.* xvi. p. 680 (1910).
† Bernfeld, *Zeit. fur Phys. Chem.* xxv. p. 46 (1898).
‡ Guinchant, *Comptes Rendus*, cxxxiv. p. 1224 (1902).
§ Aubel, *Comptes Rendus*, cxxxv. pp. 456 and 734 (1902).
‖ Koenisberger, *Zeit. Electrochem.* xv. p. 97 (1909).

stretched completely through the crystal, the circuit would be completed through the ammeter, this having the smaller resistance.

When no current is passing, the threads slowly disappear, provided that the current has not reached a maximum. This can be explained by local electrolytic action in the crystal.

It has already been stated that the current often does not fall steadily, but drops suddenly to nearly its original value. This is due to the metallic threads becoming thinner and then breaking, instead of being dissolved steadily from one end.

At high temperatures the current often rose in both directions. This could be prevented by using a very light contact of thin wire (No. 34 S.W.G). At high temperatures the pressure of the steel needle is sufficient to prevent the formation of a film at the point, which in this case is the anode, and threads are formed from the other side of the crystal. Threads will be formed very much more easily if the cathode is a sharp point, as the metal will be deposited at the point, and form the beginning of the thread; but it is conceivable that threads might form from the broad contact at the other side of the crystal when the current is large.

It was found that for any one contact the initial rate of rise of the current, and hence the rate of formation of threads, was proportional to the current. The rate of rise varied, however, for different points on the crystal. This will be discussed later. The addition of silver sulphide to the galena increased the rate of rise, while the addition of stannous sulphide decreased it. It was found that with pure lead sulphide the rate of increase per unit current with increase of temperature was constant until the transition point was reached, when it fell rapidly. With galena containing 5 per cent. stannous sulphide it increased to a maximum at 200° and then fell rapidly, showing that in neither case were threads formed above the transition point. With galena containing 10 per cent. of silver sulphide, however, the threads continued to form above the transition point. It is known that silver sulphide conducts entirely electrolytically above 179° *. This therefore is additional evidence that the rise of current is due to the electrolytic formation of metallic threads.

Unilateral Conductivity and Crystal Rectification.

There appears to be a close connexion between unilateral conductivity and the electrolytic formation of metallic threads.

* Tubandt & Eggert, *Zeit. fur Anorg. Chem.* cx. p. 196 (1920).

The rate of rise of the current varies at different points on the crystal. It was found that when rapid rise of the current occurred there was marked unilateral conductivity. The longer the current was allowed to rise, the more nearly equal became the current in the opposite directions, and the less the rectified current when subjected to an alternating potential difference.

As has already been stated, the addition of silver sulphide to the crystal increased the rate of rise; it also increased the ratio between the opposite currents and the rectifying efficiency. The addition of stannous sulphide decreased the rate of rise, the ratio between the opposite currents, and the rectifying efficiency. These facts all point to unilateral conductivity and the power of rectification being an electrolytic effect. The deposition of metal at the point produces a good metallic contact, and on reversing the current a high-resistance film is formed. Very definite evidence of the formation of this film can be obtained from the graph showing the effect of heat on the conductivity of a crystal consisting of 90 per cent. lead sulphide and 10 per cent. silver sulphide (fig. 2). It will be seen that the curve for C′ (C′ = conductivity in low-resistance direction, C″ in high) turns upwards at the transition point 133° C. In this experiment the value of C′ was read, the current immediately reversed, and C″ read. Between 130° and 170° it was found that on reversing the current the ammeter gave an instantaneous value for C″ nearly equal to C′, and then fell at once to the value shown on the graph. This meant that the current, which here increased to a very large value, deposited sufficient metal at the point of contact to cause the reverse current to take an appreciable time to remove this before the high resistance could be formed. Further, the actual strength of the current before the film was formed having increased so much, the film formed was thicker, and though C′ rose steeply, C″ actually decreased from 5 to 3 milliamps. At 170° the film was not sufficient to prevent the passage of the current, which immediately increased to 275 milliamps. C′ again decreased after the transition point, this also being due to film formation. It was also found that at about 130° to 140°, where this effect was noticed, if C′ was kept on for say 5 seconds, on reversal the current kept constant at about the same value as C′ for 6 or 7 seconds while the metal was being dissolved, and then fell suddenly as the film was formed. A similar effect was also observed in an experiment, which will be referred to later, on the variation of C′/C″ for different directions through the crystal. In one direction

where the ratio C'/C'' was very large it was found that $C''=20$ milliamps. If C'' was kept on for a few seconds and the current then reversed, C' kept nearly constant for a short time and then rose suddenly to 300 milliamps, showing that a high-resistance film was formed when the metal point was the anode, and was removed on reversing the current, the current rising suddenly when the disappearing film was replaced by metallic contact. These observations appear to give definite evidence that a high-resistance film is formed electrolytically when the point is the anode, and metallic contact when the point is the cathode.

It has been stated that for crystals of lead sulphide and lead sulphide containing 5 per cent. of stannous sulphide $\frac{dC}{dT}\cdot\frac{1}{C}$ (C = current, T = time) falls rapidly above the transition temperature, while it does not do so for lead sulphide containing 10 per cent. of silver sulphide. It was also found that the ratio C'/C'' decreased above the transition point for lead sulphide and lead sulphide containing 5 per cent. stannous sulphide, but did not do so for lead sulphide containing 10 per cent. silver sulphide.

It was found for lead sulphide containing 5 per cent. stannous sulphide and occasionally for pure lead sulphide that the high-resistance direction was not always the same; but when the high-resistance direction was such that the point was the cathode, the difference between the two conductivities was very small; when marked unilateral conductivity occurred, the point was invariably the cathode. It appears that slight unilateral conductivity occurs in these crystals in a direction such that it cannot be explained by the above reasoning. In the following crystals the direction of the rectified current is also such that the point is positive*: molybdenite (MoS_2), galena (PbS) (natural), zincite (ZnO), iron pyrites (FeS_2), cassiterite (SnO_2), and carborundum (SiC). In all these it is interesting to note that the metals readily form amphoteric electrolytes.

Several observers† have noticed a hysteresis effect when the characteristic curve is traced by the steady-current method. On reversing the current and completing the cycle of applied potential, the curve was found to enclose an area. This is explained by the fact that metallic threads are formed, these having to be dissolved again on reversal of the current, thus producing a hysteresis effect.

One of the most puzzling facts in connexion with the

* Strachan, 'Wireless World,' xiv. p. 397 (1924).

† Pierce, Phys. Rev. xxv. p. 31. Goddard, Phys. Rev. xxxiv. p. 423. Coursey, Proc. Phys. Soc. xxvi. p. 105.

conductivity of crystals is the different behaviour obtained at different parts of the crystal. The rate of rise of the current, the magnitude of the current, the ratio of the conductivities in opposite directions, and the rectifying power or "sensitivity" vary greatly at different parts of crystal surface. This effect is particularly noticeable in the case of a crystal with well-defined faces, and much less so with one with a granular structure and innumerable small facets, when the results are more consistent.

It has been shown by Tubandt * that in solid electrolytes such as the silver halides and silver sulphide the current is carried entirely by the positive ion. Lead chloride differs in that the current is carried by the negative ion. One set of ions in these solids forms a fixed framework through which the other ions move with considerable facility.

Thus in silver sulphide, and most probably in galena, any current which is carried electrolytically will be carried by the metal ion, which will move through a fixed framework of the sulphide ions towards or away from the metallic point.

The structure of a great many crystals has now been determined by several workers. Lead sulphide belongs to the regular system, and usually crystallizes in cubes. It has a simple cubic structure.

In a crystal having such a structure the (100) planes of the crystal each contain both lead and sulphur atoms, the (110) planes will likewise contain lead and sulphur atoms, but the (111) planes, however, will consist alternatively of lead or sulphur atoms

Consider what occurs when the current is being conducted to the metal point along (100) or (110) planes. The metal ions will move towards the point through a fixed framework of sulphur ions ; but as they move towards the point they will come into collision with the sulphur ions, and their progress will be retarded. On the other hand, if the current is being conducted along (111) planes, the metal ions will be in one plane and the sulphur ions in the other, and the metal ions will move straight towards the point without colliding with the sulphur ions. Hence, when the current is carried along (111) planes, the metal ions will move with greater facility.

Considering an alternating current passing through the crystal when the current is passing in a direction such that the point is the cathode, metal ions move through the sulphur ions towards the point, giving a metallic contact. On the reversal of the current these ions move away again, leaving a film of sulphur. They will do this with greater facility when the current is carried along planes such that the ions

* Tubandt, *Zeit. fur Electrochem.* xxvi. p. 358 (1920).

do not collide, and we should then expect to get maximum rectification.

It has been stated by R. Ettenreich * that the time of reaction in crystal rectifiers is less than 10^{-6} second, and that this makes electrolytic polarization theories involving comparatively slow molecular movements untenable. In the theory stated above, the film is present continually and the metal ions oscillate to and fro through permanent channels, giving metallic and non-metallic contact alternatively. If the time of reaction is of the order stated by Ettenreich, it is quite in keeping with atomic oscillations of this kind.

Fig. 4.

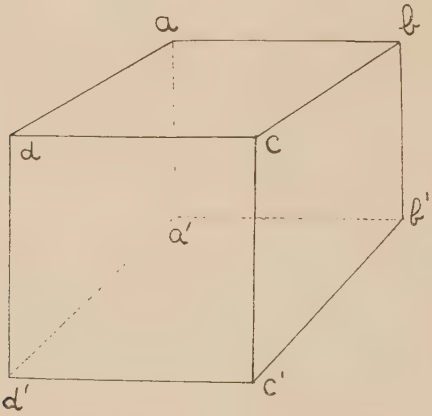


Diagram of a cubic crystal of lead sulphide.

Since the addition of 10 per cent. of silver sulphide increases the rate of formation of metallic threads so considerably, it increases the fraction of the current conducted electrolytically to the same extent, which means that only a small fraction of the current is conducted electrolytically in pure lead sulphide. This fraction causes the alternate metallic and non-metallic contact which has been described, and this rectifies, in addition to itself, that part of the current which is conducted metallically. When the ions move without collision a greater fraction of the current is carried electrolytically. Hence the fraction of the current carried electrolytically varies according to the plane along which the current is passing through the crystal.

Fig. 4 represents a cubic crystal of lead sulphide. According to the theory which has been stated, maximum

* R. Ettenreich, *Phys. Zeit.* xxi. p. 208 (1920).

unilateral conductivity (or allied phenomena such as rectification) should be a maximum when the current is carried along (111) planes, *e. g.* when the current passes from *a* to *c* or *b* to *c'*. It should be a minimum when the current passes along (100) or (110) planes, *e. g.* from *a* to *b* or from *a* to *c'*.

With a crystal of pure synthetic lead sulphide, as near a perfect cube as could be obtained, the following results for the ratio of the conductivities in opposite directions were the mean of a number of determinations :—

Current passing from	*a* to *b*	*a* to *c'*	*a* to *c*
Mean ratio, C'/C'' ...	1·03 : 1	1·23 : 1	15·9 : 1

These results show that when the current is carried along (111) planes the unilateral conductivity is very much greater than when the current is carried along (110) or (100) planes. This entirely bears out the theory which has been stated.

When a crystal is rectifying high-frequency currents, the ions actually causing rectification will be confined to an extremely thin surface layer at the point of contact, and hence the degree of rectification will depend on the plane along which the current is carried in the surface layer of crystal at the point of contact. Thus with a crystal having an irregular surface maximum rectification will occur at those points where the surface at the point of contact is at such an angle that the current is carried along the (111) planes.

Silver sulphide increases the rectifying power of lead sulphide because it increases the amount of electrolytic conduction, thus increasing the number of ions oscillating in the surface film, and hence the efficiency of the metallic and non-metallic contact. The effect of stannous sulphide in decreasing the rectification is probably due to the fact that it is not isomorphous with lead sulphide, although partially soluble in it. It has a different atomic structure, and its space-lattice will be superimposed upon that of the lead sulphide. Its atoms will therefore obstruct the path of the ions moving in the (111) planes, and hence decrease rectification.

A small applied potential in the same direction as the rectified current improves rectification in most crystals. This is probably due to the fact that the applied potential will assist the formation of metallic threads, but will not be sufficient to prevent the formation of the high-resistance film. Thus it will increase the conductivity of the crystal in the low-resistance direction, but not affect it in the high. In the

case of lead sulphide the crystal has a low resistance and the threads are formed rapidly, hence an applied potential does not make much difference. It is a slight advantage, however, but it should be less than one volt. As has been shown, a large potential will cause the formation of permanent threads which destroy rectification.

Strachan * observed that in the rectification of high-frequency currents, when the contact is a loose one and the metal point made from fine wire, oscillation of the point occurs. If a sudden strong current is sent through the crystal, the contact is completely broken. This is easily understandable on the above theory, and is caused by the surging to and fro of the ions. When a strong current is suddenly applied, the amount of metal forced against the point is sufficient actually to move it.

Although in the past electrolytic theories have received little support, and have been subjected to much criticism, the above modification of the old electrolytic theory is based upon experimental evidence, and explains several phenomena which could not be satisfactorily explained by other theories, such as the variation of the rectifying power over the surface of the crystal or "sensitive spots," and the effect of silver sulphide in increasing the rectifying power of crystals of lead sulphide.

Summary.

(1) Galena has a transition point at 160° C., there being an increase of conductivity at this temperature.

(2) Addition of silver sulphide increases the rise of conductivity at the transition point.

(3) Passage of a direct current through galena, the negative contact being a point, is accompanied by the electrolytic formation of metallic threads. This is increased by the addition of silver sulphide and decreased by the addition of stannous sulphide.

(4) Unilateral conductivity, rectification, and electrolytic formation of threads are closely connected.

(5) When the point at the contact is positive a high-resistance film is formed.

(6) Unilateral conductivity and rectification can be explained from consideration of the structure of crystals, and by the fact that in solid electrolytes the current is carried entirely by one set of ions, the other set forming a fixed framework.

* Strachan, 'Wireless World,' xiv. p. 424 (1924).

(7) In rectification the metal ions oscillate to and fro through fixed channels of sulphur ions, giving metallic and non-metallic contact alternately.

(8) The variation of rectifying properties at different points on the crystal surface can be explained by the fact that the metal ions can move without collision in some planes of the crystal but not in others.

(9) Experimental determinations of the ratio of C'/C'' for different directions through the crystal are completely in accordance with this theory.

(10) Hitherto unexplained phenomena connected with crystal rectification can be explained by this theory.

In conclusion, the author wishes to thank Mr. W. H. Patterson, M.Sc., for his continual interest and help in connexion with this work.

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LXXIII. *Space-Charge and Thermionic Currents.* *By* Wm. S. Kimball *.

THE effect of space-charge upon thermionic currents in high vacuum was first treated theoretically by Child † and Langmuir ‡. If the accelerating field was sufficient to cause saturation, assuming the initial velocity of the electrons to be zero, they found that this maximum current varied with the three-halves power of the potential difference between the anode and cathode, and that the potential varied with the four-thirds power of the distance from the cathode. Since then the theory has been extended by Laue §, Richardson ‖, Epstein ¶, Fry **, Langmuir ††, and others, taking account of initial velocities or special cases of interest; and Bridgman has treated the theory in its bearing on contact electromotive forces. No attempt seems to have been made to analyse the potential function into its two component parts: the impressed potential and the space charge potential, the former being the potential that would be present

* Communicated by the Author.
† Phys Rev. xxxii. p. 492 (1911). ‡ Phys. Rev. ii. p. 450 (1913).
§ *Jahrbuch d. Rad. u. Elek.* xv. p. 205 (1918).
‖ Em. of Elec. fr. Hot Bodies.
¶ *Ber. d. Deut. phys. Ges.* xxi. p. 85 (1919).
** Phys. Rev. xvii. p. 441 (1921).
†† Phys. Rev. xxi. p. 419 (1923).

between the electrodes in case the space-charge were removed to infinity. The present paper is a critical study of the relations between these two parts of the resultant potential, showing the rôle each plays in the general theory. Attention is restricted to the simple case of currents where the initial velocity of the electrons, that is at the cathode, is zero. The case of parallel plane electrodes is considered in some detail. A special study of the boundary values of the charge density and electron velocity at the anode shows how the equation for the current between parallel plane electrodes may be derived without integrating the differential equation of the potential function. Conditions are established which the exact equation for the current between cylindrical electrodes must satisfy, it being pointed out that the approximate expression given by Langmuir * satisfies them.

§ 1. It is well known that the potential distribution between parallel planes having empty space between them is of the form : $V'=Ex$, where E is the force constant, and that it satisfies Laplace's equation. Since the potential function is a scalar point function, the resultant potential when space charge is present may be separated into its two parts added algebraically : $V=V'+V''$, where V'' is the space-charge potential function. The well-known equations of condition then take the form :

$$1/2\, mv^2=e(V'+V'')=(Ex+V'')e=Ve. \quad . \quad . \quad (1)$$

$$i=\rho v. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{d^2V''}{dx^2}=4\pi\rho. \quad . \quad . \quad . \quad . \quad . \quad . \quad , \quad . \quad , \quad . \quad (3)$$

These are the same as those given by Langmuir except for the immaterial change of dropping V' from (3) since its Laplacian is zero. Thus (3) refers to either the space-charge potential or to the resultant potential, but it cannot refer to the impressed potential whose Laplacian vanishes.

§ 2. When ρ and v are eliminated from these three equations we have :

$$\frac{d^2V''}{dx^2}=2\pi\sqrt{2}\sqrt{\frac{m}{e}}\frac{i}{\sqrt{Ex+V''}}. \quad . \quad . \quad . \quad (4)$$

Use $2\left(E+\frac{dV''}{dx}\right)$ as integrating factor, and integrate :

$$\left(\frac{dV''}{dx}\right)^2+2E\frac{dV''}{dx}+E^2=8\pi i\sqrt{\frac{2m(Ex+V'')}{e}}. \quad (5)$$

* Phys. Rev. xiv. p. 306 (1919).

Here E^2 is the constant of integration, so chosen to give the condition for space-charge limited currents : at the cathode where each potential is zero, the resultant force is zero : $\frac{dV''}{dx} = -E$. Taking the square root of (5) and integrating and solving for i and V gives

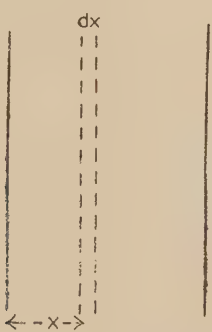
$$i = \sqrt{\frac{2e}{m}} \frac{1}{9\pi} \frac{(Ex+V'')^{3/2}}{x^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$V = Ex + V'' = cx^{4/3}, \text{ where } c = (9\pi i)^{2/3}(m/2e)^{1/3}. \quad (7)$$

These equations show that the resultant potential varies with the four-thirds power of the distance from the cathode, and that the space-charge limited current varies with the three-halves power of the resultant potential.

§ 3. *Force due to Space-Charge.*—It is well known that an infinite plane carrying a charge of uniform density, and with no other charges or conductors in its neighbourhood, will exert a force independent of the distance from the plane. If parallel plane conductors are placed at different distances from it, on each side of the uniformly charged plane, there

Fig. 1.



will be induced upon the two conducting planes charges whose density is inversely proportional to their distance from the charged plane between them. If the conductors are at zero potential, the induced charge will be the sole charge on them, and being proportional to charge, the force on each side of the charged plane will thus be inversely proportional to the distance to the parallel conductor. The assumption that the parallel plane electrodes are at zero potential restricts attention to the force due to the space-charge on this plane between them. That the force is

inversely proportional to the distance from the electrodes is the outcome of the fundamental principle involved: that equal work is required to take unit charge from either zero potential electrode to the charged plane. If σ_2 is the surface-charge density induced on the cathode and σ_1 is the surface-charge density induced on the anode of a plane of thickness dx and charge density ρ at distance x from the cathode, then the force between this plane and the anode is $4\pi\sigma_1$, and the force anywhere between this plane and the cathode is $-4\pi\sigma_2$. It is noteworthy that the direction is reversed as well as the magnitude of the force operating on an electron changed, as the latter passes through the plane in question.

The space between parallel plane electrodes may be considered as composed of a series of such planes of thickness dx and charge density ρ which latter is constant over each plane but differs for different planes. The sum of the forces due to these planes is the total force due to the space-charge:

$$\frac{dV''}{dx} = \int_0^x 4\pi\sigma_1 - \int_x^b 4\pi\sigma_2, \quad . \quad . \quad . \quad . \quad (8)$$

where the σ's are functions of x. The first definite integral gives the sum of the forces due to the several layers of charge behind an electron at distance x from the cathode, that is, it is the total force driving unit charge across. The second integral gives the total force driving unit charge back towards the cathode. Force exerted by the impressed potential is, of course, not included in (8).

Since the potential difference due solely to its own charge between a particular charged plane and each electrode at zero potential is the same, we have a condition on the σ's:

$$4\pi\sigma_2 x - 4\pi\sigma_1(b-x) = 0, \quad \text{or} \quad \sigma_2 x = \sigma_1(b-x), \quad . \quad (9)$$

where b is the distance between electrodes. A second condition on them is

$$\sigma_1 + \sigma_2 = \rho\, dx. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The dx appearing in (10) reveals the difference in dimensions of the surface and volume densities. Solving (9) and (10):

$$\sigma_1 = \rho\frac{x}{b}\, dx\ ;\ \sigma_2 = \rho\frac{(b-x)}{b}\, dx. \quad . \quad . \quad . \quad (11)$$

Substituting these values in (8) gives

$$\frac{dV''}{dx} = \int_0^x 4\pi\rho \frac{x}{b}\, dx - \int_x^b 4\pi\rho \frac{b-x}{b}\, dx. \quad . \quad (12)$$

§ 4. *Boundary Condition upon Force due to Space-Charge.*—If the velocity of the electrons emitted at the cathode is assumed to be zero, then the condition for space-charge limited currents is that the resultant force there due to both space-charge and impressed voltage shall be zero. Since the impressed force is constant between the parallel plane electrodes and equal to E, the boundary condition on the space-charge force at the cathode requires this force to be equal to $-E$. Combining the terms of (12) that involve x explicitly, we may write:

$$\frac{dV''}{dx} = \int_0^b 4\pi\rho \frac{x}{b}\, dx - \int_x^b 4\pi\rho\, dx = D - \int_x^b 4\pi\rho\, dx. \quad (13)$$

Here the first term on the right, being a constant, is set equal to D. The value of the space-charge force at a particular distance from the cathode is given by (13) or (12) by giving to the x appearing as a limit in the definite integrals the particular value of the distance in question. Setting x equal to zero in (13) gives

$$\left(\frac{dV''}{dx_0}\right) = D - \int_0^b 4\pi\rho\, dx = -E. \quad . \quad . \quad . \quad (14)$$

This is the boundary condition on the space-charge force at the cathode.

§ 5. *The Space-Charge Potential Function.*—This may be expressed as an integral of (12) or (13):

$$V'' = \int_0^x \int_0^x 4\pi\rho \frac{x}{b}\, dx\, dx - \int_0^x \int_x^b 4\pi\rho \frac{b-x}{b}\, dx\, dx$$

$$= Dx - \int_0^x \int_x^b 4\pi\rho\, dx\, dx. \quad . \quad (15)$$

Equation (9) states that the work due to the particular plane referred to upon unit charge in crossing from cathode to anode is zero. This is the conservation of energy. Equation (15) is the work required to take unit charge from the cathode to distance x due to all of the space-charges. If the upper limit of (15) be set equal to b, the work represented by it will be the sum of such works as represented by (9) for all the space-charge plane layers between the

electrodes. Since the work due to each layer of charge upon unit charge crossing to the anode sums up to zero, the work due to all the layers together must sum up to zero. Thus when the upper limit of (15) is b, V'' must be identically zero. This may be shown by integrating the 2nd term by parts:

$$V_b'' = Db - \int_0^b \int_x^b 4\pi\rho\, dx\, dx = Db - \left[\left(x\int_x^b 4\pi\rho\, dx\right)_0^b + \int_0^b 4\pi\rho x\, dx\right] = 0. \quad (16)$$

The expression in the parenthesis vanishes when the limits 0 and b are substituted, and the last integral is shown by (13) to be equal to $-Db$, so that (16) vanishes identically. This boundary condition on the space-charge potential function is inherent in electrostatics and conservation of energy.

§ 6. *Application of Boundary Conditions for Parallel Plane Electrodes.*—The relations established in § 5 on the space-charge potential may be applied to (7) to get a relation between the constant c appearing in (7) and E, the impressed force. Since $V = V' + V''$, and V'' is zero at the anode, the resultant potential V is at the anode: $V = V' = Eb$. Thus by (7)

$$V = V' = Eb = cb^{4/3}.$$

Hence:

$$c = E/b^{1/3}, \quad \ldots\ldots\ldots\ldots \quad (17)$$

and (7) takes the form:

$$V = Ex + V'' = \frac{Ex^{4/3}}{b^{1/3}}; \quad \ldots\ldots\ldots \quad (18)$$

hence:

$$V'' = \frac{Ex^{4/3}}{b^{1/3}} - Ex. \quad \ldots\ldots\ldots \quad (19)$$

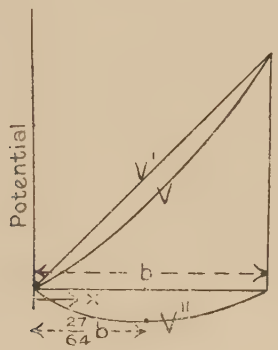
$$\frac{dV''}{dx} = \frac{4}{3}E\left(\frac{x}{b}\right)^{1/3} - E. \quad \ldots\ldots\ldots \quad (20)$$

$$\rho = \frac{E}{9\pi b^{1/3}x^{2/3}} = \frac{1}{4\pi}\frac{d^2V''}{dx^2}. \quad \ldots\ldots\ldots \quad (21)$$

The minimum value of V'' occurs where by (20) the force is zero. It occurs at $x = \frac{27}{64}b$, as shown in the graph.

The absolute magnitude of V″ is here 1/4 that of the impressed potential V′ for this value of x. From the cathode out to this point the space-charge opposes the motion of the electrons, but between this point and the anode it expedites their motion.

Fig. 2.



If the potential function appearing in (6) is replaced by (18), the space-charge limited current equation takes the form:

$$i=\sqrt{\frac{2e}{m}}\left(\frac{1}{9\pi}\right)\frac{E^{3/2}}{\sqrt{b}}=\sqrt{\frac{2e}{m}}\cdot\frac{1}{9\pi}\frac{(Eb)^{3/2}}{b^2}\cdot\quad\cdot\quad\cdot\quad(22)$$

It is noteworthy that this expression is free from the variable x. Its form thus brings out the fact that the current per square centimetre cross-section is independent of the distance of this square centimetre from either electrode, being a constant for changes of x. Since $i=\rho v$, and i is independent of x, the exact equation (22) may be written down if the values of ρ and v at the anode are given: (1) and (18) give v and (21) gives ρ:

$$v_b=\sqrt{\frac{2e}{m}}\sqrt{Eb}\,;\quad\text{and}\quad\rho_b=\frac{E}{9\pi b}\cdot\quad\cdot\quad\cdot\quad(23)$$

The problem of obtaining these boundary values of v and ρ is theoretically a simpler problem than that of obtaining complete information about distribution of potential and charge between electrodes, which is supplied by solution of the differential equation with application of boundary conditions as set forth above. Thus the problem of deriving the exact expression for the saturation current that is constant

between the electrodes is theoretically simpler than that of solving the differential equation for space-charge distribution.

§ 7. *Boundary Condition upon the Charge Density.*—It can be shown directly from electrostatics that $\rho_b = \lambda \frac{E}{b}$, where λ is a pure number, is the expression for the charge density at the anode. To prove this consider equation (3). Since V and V″ are each proportional to the constant E, this equation shows that ρ must also be so. Since b is the only geometrical constant describing the configuration of the electrodes, we may write: $\rho = \lambda E f(b)$. It is well known that electrostatic force is of the same dimensions as surface-charge density, so that volume charge density or ρ must be of dimensions $\frac{E}{L}$ where L stands for length. Since b is the only length involved in the configuration of parallel plane electrodes, it is evident that $f(b) = \frac{1}{b}$ and $\rho_b = \lambda \frac{E}{b}$, which was to be proved.

The value of the resultant potential at the anode, $V = V' = Eb$, together with (1) gives: $v_b = \sqrt{\frac{2e}{m}} \sqrt{Eb}$ for the velocity of the electrons there. Multiplying this by $\rho = \lambda \frac{E}{b}$ established in this section gives

$$i = \lambda \sqrt{\frac{2e}{m}} \frac{E^{3/2}}{\sqrt{b}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

This expression for the space-charge limited current is the same as (22) except for a numerical factor, and is obtained without integrating the differential equation (3).

The relations (17)–(21) are obtained from the boundary condition established in § 5 on the space-charge function V″, but if (21) is used to carry out the integrations of § 4, the above relations are seen to be consistent with the boundary conditions established there on the force.

§ 8. *Space-charge Force for Cylindrical Electrodes.*—It is well known in electrostatics that the charge on an insulated hollow cylinder is on the outside, and that within there is uniform potential and no force or charge. If, however, a concentric conducting cylinder within the outer cylinder is grounded, an equal and opposite charge is induced upon the inner cylinder, and the charge on the outer cylinder is transferred from the outside to the inside, and a field is set

up between the two cylinders. Likewise if the two cylinders are connected to the two poles of a battery a field is set up between them and the distribution of potential between them is given by $V' = 2k \log \frac{r}{a}$, where k is the charge per unit length on one of the cylinders, and a is the radius of the inner one, which may be taken as the cathode, with zero potential, and r is the distance from any point between the cylinders to their axis.

Assume a thermionic current in a steady state flowing between these electrodes. The space between them wi l contain a series of concentric cylindrical layers of charge. Each layer has uniform distribution of charge upon it, but different layers have different density of charge. Consider a layer of thickness dr and density ρ and distance r from the axis. This layer of negative electricity will induce an equal positive charge on the two electrodes, but not in general an equal amount on each of the two electrodes surrounding the layer. Let σ_1 be the surface density of charge on the outside of the layer in question, and σ_2 that on the inside of this layer. We have :

$$\sigma_1 + \sigma_2 = \rho\, dr \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The charge density induced on the anode will then be $\sigma_1 \frac{r}{b}$ and that induced on the cathode will be $\sigma_2 \frac{r}{a}$, since the areas of the anode and cathode differ from the area of the layer of charge by the indicated proportions. The force due to the layer between the anode and the layer in question is $\frac{4\pi r \sigma_1}{r_0}$, and the force between the cathode and the layer is $-\frac{4\pi r \sigma_2}{r_0}$, where r_0 refers to the place at which the force is measured, being greater than r in the first expression and less in the second. If the potential at each electrode is assumed to be zero, attention is restricted to the effect of the space-charge layer. Equal work will be required to bring unit charge from either electrode to this layer. We have then :

$$\int_r^b \frac{4\pi r \sigma_1 dr_0}{r_0} = \int_a^r \frac{4\pi r \sigma_2 dr_0}{r_0},$$

where r and the σ's are constants for the integration.

$$4\pi r \sigma_2 \log \frac{r}{a} + 4\pi r \sigma_1 \log \frac{r}{b} = 0. \quad . \quad . \quad (26)$$

$$\sigma_2 \log \frac{r}{a} = -\sigma_1 \log \frac{r}{b} \quad . \quad . \quad . \quad . \quad (27)$$

Solving (25) and (27) for σ_1 and σ_2 gives

$$\sigma_1=\rho\frac{\log\frac{r}{a}}{\log\frac{b}{a}}dr \quad \text{and} \quad \sigma_2=\rho\frac{\log\frac{b}{r}}{\log\frac{b}{a}}dr. \quad . \quad . \quad . \quad (28)$$

The total space-charge force will be the sum of the forces due to each cylindrical layer of charge :

$$\frac{dV''}{dr}=\frac{4\pi}{r}\int^{r} r\sigma_1-\frac{4\pi}{r}\int_{r}^{b} r\sigma_2=\frac{4\pi}{r}\int_{a}^{r}\frac{r\rho\log\frac{r}{a}dr}{\log\frac{b}{a}}$$

$$-\frac{4\pi}{r}\int_{r}^{b}\frac{r\rho\log\frac{b}{r}dr}{\log\frac{b}{a}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

§ 9. *Boundary Conditions on Force in case of Cylindrical Electrodes.*—Equation (29) may be written :

$$\frac{dV''}{dr}=\frac{4\pi}{r}\left(\int_{a}^{b}\frac{r\rho\log\frac{r}{a}}{\log\frac{b}{a}}dr-\int^{b}\rho r\,dr\right); \quad . \quad . \quad . \quad (30)$$

or

$$\frac{dV''}{dr}=\frac{4\pi}{r}\left(\int_{a}^{b}\frac{r\rho\log\frac{r}{b}}{\log\frac{b}{a}}dr+\int_{a}^{r}\rho r\,dr\right). \quad . \quad . \quad . \quad (31)$$

The condition for space-charge limited currents when the initial velocity of the electrons is assumed to be zero is that the force due to the resultant potential be zero at the cathode where $r=a$. This requires that the space-charge force be equal in magnitude and opposite in sign to the force due to the impressed potential at the cathode. This latter force is $\frac{2k}{a}$, so that the boundary condition on the space-charge force is :

$$\frac{dV''}{dr}=-\frac{2k}{a}. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The second integral of (31) evidently vanishes when $r=a$,

and comparison of the first term of (31) taking $r=a$ with (32) gives the boundary condition :

$$k=-2\pi\int_a^b \frac{r\rho\log\frac{r}{b}}{\log\frac{b}{a}}\,dr=+2\pi\int_a^b r\sigma_2. \quad . \quad . \quad . \quad . \quad (33)$$

The first term of (30) evidently gives the force at the anode due to the space-charge potential function.

§ 10. *Boundary Conditions on the Space-charge Potential for Cylindrical Electrodes.*—Taking account of (33) the integral of (31) may be expressed :

$$V''=-2k\log\frac{r}{a}+\int_a^r\frac{4\pi dr}{r}\int_a^r \rho r\,dr. \quad . \quad . \quad (34)$$

The conservation of energy equation (26) states that the work due to a single layer of space-charge when unit charge is taken from cathode to anode is zero. If the upper limit of V'' in (34) be taken $r=b$ then this equation will represent the sum of such works for all space-charge layers, and must therefore be identically zero. This may be shown by integrating the second term of (34) by parts, taking the upper limit $r=b$:

$$V_b''=-2k\log\frac{b}{a}+4\pi\left(\log\frac{b}{a}\int_a^b \rho r\,dr-\int_a^b\log\frac{r}{a}\rho r\,dr\right)=0. \quad (35)$$

The last two terms are seen by (33) to be equal to $2k\log\frac{b}{a}$ which cancels the first term. Thus $V_b''=0$ is the boundary condition on the space-charge potential. Since $V=V'+V''$, this condition is equivalent to :

$$V_b=V_b'=2k\log\frac{b}{a}. \quad . \quad . \quad . \quad . \quad . \quad (36)$$

§ 11. *The Space-Charge Limited Current.*—The current given by equation (2) for parallel plane electrodes and by $i=2\pi r\rho v$ for cylindrical electrodes is constant between the electrodes. Likewise for any shaped electrodes $i=a\rho v$ is constant between them if a is the variable area of cross-section of the tube of flow, or tube between electrodes containing all the current under consideration. The values of ρ and v at the anode, together with the area "a" of the tube which is determined by the geometry of the electrodes, are thus all that is

required to set up the equation of the saturation current in terms of the constants of the electrodes in question. The value of v at the boundary is given by equation (1) using the boundary condition established for $V_b = V_b'$: equation (36) for cylindrical electrodes. For a given pair of equipotential electrodes, then, all factors that make up the saturation current are known except ρ_b the charge density at the anode. To obtain this, it would not seem necessary to solve Poisson's equation for the electrodes in question. This method gives the distribution of potential as well as force and charge density *between the electrodes*, a result very much more comprehensive than obtaining merely the charge density at the anode. The problem of obtaining the exact expression for the space-charge limited current in terms of the impressed voltage, and the geometrical constants of the configuration of the electrodes, is therefore distinct from the problem of solving the differential equation obtained by replacing the charge density appearing in Poisson's equation by its value in terms of V by means of (1) and (2). It is distinct and possibly simpler than this latter problem to the extent that obtaining the boundary value of the charge density at the anode is distinct from obtaining complete information as to distribution of charge density, force, and potential everywhere between the electrodes.

§ 12. *Boundary Conditions on the Charge Density for Cylindrical Electrodes.*—The current expressed by

$$i = 2\pi r \rho v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

is constant between the electrodes. Equations (36) and (1) give the velocity of electrons at the anode:

$$v_b = \sqrt{\frac{2e}{m}} \sqrt{2k \cdot \log \frac{b}{a}} \quad . \quad . \quad . \quad . \quad (38)$$

If the expression for ρ_b the charge-density at the anode can be obtained in terms of k and a and b, on which it depends, this value of ρ, together with (38), will give the current per unit length of electrode when substituted in (37). The writer has been unable to obtain this expression for ρ_b directly from electrostatics for the cylindrical electrodes, as done in § 7 for parallel plane ones. But the choice of ρ_b is restricted by the following boundary conditions:

(*a*) $\rho_b = k f(a, b)$: it is proportional to k.

This follows from Poisson's equation in cylindrical coordinates, because the first and second derivates of V'' appearing

in the left-hand side of this equation are each directly proportional to k, the charge per unit length induced on the electrodes by the impressed potential. Thus ρ appearing as a factor of the right-hand member of Poisson's equation must be proportional to k also. Since a and b are the only geometrical constants involved, ρ_b will depend on some function of them as indicated above.

(*b*) $\mathrm{P}=\lambda\frac{k}{\mathrm{L}^2}$.

Here L means any length. This condition follows from dimensional considerations since ρ_b is charge per unit volume, and k is charge per unit length. λ is a pure number.

(*c*) When $a=b=\infty$, $\rho_b=\lambda\frac{\mathrm{E}}{b-a}$.

When the radii of curvature of the cylindrical electrodes are infinitely large, we have parallel plane electrodes, so that ρ_b must reduce in this case to expressions found in § 6, and § 7, which are equivalent to (*c*) when $b-a$ is the distance between electrodes.

(*d*) When $a=0$, $\rho_b=0$.

As the size of the cathode approaches zero, the current emitted will evidently approach zero, and hence the charge density at the anode will approach zero.

§ 13. *Form of Expression for Charge Density satisfying the Conditions of* § 12.—It is not difficult to show that the above conditions are satisfied by any ρ_b of the form :

$$\rho_b=\lambda\frac{k}{b^2 f\left(\log\frac{b}{a}\right)}, \quad \ldots\ldots \quad (39)$$

where $f\left(\log\frac{b}{a}\right)$ refers to any function of $\log\frac{b}{a}$ expressible as a power series in $\log\frac{b}{a}$, whose constant or zero power term is lacking, and also whose first power term is present, such as simply $\log\frac{b}{a}$ itself, or $\left(\frac{b}{a}-1\right)$.

The current equation of Langmuir :

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\frac{\mathrm{V}^{3/2}}{b\beta^2},$$

where

$$\beta=\log\frac{b}{a}-\frac{2}{5}\left(\log\frac{b}{a}\right)^2+\frac{11}{120}\left(\log\frac{b}{a}\right)^3\cdots$$

shows in view of (36), (37), and (38) that his ρ involved in this current equation is of the form (39).

The writer is much indebted to Prof. W. F. G. Swann and Mr. E. S. Akeley of Chicago for valuable criticism and discussions.

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LXXIV. *On Molecular Diameters.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in your November number of 1924 on "The Determination of Molecular Diameters," Mr. Sergius Mokroushin deduces a formula for the diameter which includes the following reasoning: The internal heat of vaporization of a gram-molecule is equal to the product of the surface-tension and the surface of all its molecules. The molecules are thus assumed to be liquid droplets having the same surface-tension as the liquid itself. In a paper just published * I have calculated molecular diameters starting also from a relation between heat of vaporization and surface-tension, using the modern point of view on constitution of matter.

All methods of this determination, which are founded on phenomena caused by molecular collision, give values of the diameter depending upon the momentum of the colliding molecules. The greater their velocity is and the higher consequently (in cases to be discussed) the corresponding temperature is, the smaller such a diameter turns out. It is called recently "Stossdurchmesser" in German, which may be translated by "collisional diameter." The method I used gives collisional diameters and was employed in order to determine them at a temperature as low as possible.

It is now shown † that surface-tension consists of a statical

* *Zeitschr. f. Physikalische Chemie*, cxiv. p. 114 (1925).

† Madelung, *Physikalische Zeitschr.* xiv. p. 729 (1913). Born und Courant, *Physikalische Zeitschr.* xiv. p. 731 (1913).

portion χ, independent of molecular motion, and of a kinetic portion dependent upon temperature and vanishing in the limit to the absolute zero. Therefore we may write for χ_0, the statical portion at the absolute zero, using the relation of Ramsay and Eötvös

$$\chi_0 = \frac{2{\cdot}1 T_K}{V_0^{2/3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T_K is the critical temperature and V_0 the molecular volume at the absolute zero.

As to the constitution of the molecule we assume that it is in case of non-associating substances an electric quadruple. That is a neutral aggregate of positive and negative charges whose centres coincide in absence of a field. In a field f it is deformated and acquires a momentum αf, α being a molecular constant. τ is also a molecular constant determined by the configuration of the charges. These assumptions were made by Debye * in order to explain the v. d. Waals forces. In the same paper he calculates the statical portion of surface-tension as the mechanical work required to build up the unit area of the surface, not regarding it as a monomolecular layer, and finds

$$\chi = \frac{3\pi}{8} \frac{\alpha \tau^2 n^2}{s^4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n is the molecular density and s the molecular diameter considered as collisional as follows from Debye's reasoning. He determines also A, the internal heat of vaporization for one gram-molecule in C.G.S.-units, by the same quantities. From his formula we obtain

$$A = \frac{6\pi}{5} \frac{\alpha \tau^2}{s^5} n^2 V, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where V is the molecular volume at boiling-point.
From (2) and (3) we obtain

$$s = 3{\cdot}2 \frac{\chi V}{A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Since from (2) $\chi \sim n^2 \sim \frac{1}{V^2}$ we get from (4) by use of (1)

$$s = 6{\cdot}72 \frac{T_K}{A} \frac{V_0}{V} V_0^{1/3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* *Physikalische Zeitschr.* xxi. p. 178 (1920).

Assuming the closest packing of molecules at the absolute zero, so that $V_0 = \frac{L}{\sqrt{2}} s^3$, and putting $V = \frac{M}{D}$,

$$\Lambda = M\lambda_i 4{\cdot}18 \,.\, 10^7,$$

where

D = the density of the liquid at boiling-point,

M = the molecular weight,

λ_i = the internal heat of vaporization for one gram in cal.

L = Loschmidt's number, the number of molecules in one gram-molecule,

we find from (5) for the molecular diameter in centimetres

$$s \,.\, 10^8 = \sqrt[3]{0{\cdot}184 \frac{M^2 \lambda_1}{T_K D}}. \quad . \quad . \quad . \quad . \quad (6)$$

The following table gives values for s calculated by (6) and also values for s^*, the diameter on the dynamical theory

TABLE I.

Substance.	$s \,.\, 10^8$.	$s^* \,.\, 10^8$.	$\frac{s}{s^*}$.
Helium	3	1·9	1·6
Hydrogen	3·1	2·3	1·3
Nitrogen	3·9	3·1	1·3
Carbon monoxide	3·9	3·2	1·2
Argon	3·6	2·7	1·3
Oxygen	3·6	2·9	1·2
Carbon dioxide	4·0	3·2	1·3
Nitrous oxide	4·0	3·1	1·3
Methyl chloride	4·5	3·4	1·3
Chlorine	4·3	3·7	1·2
Iso-pentane	6·4	4·5	1·4
Ethyl ether	6·2	4·8	1·3
Acetone	5·8	3·8	1·5
Methyl acetate	5·8	3·8	1·6
Ethyl acetate	6·4	4·2	1·5
Chloroform	5·7	4·8	1·5
Benzene	5·9	4·1	1·4
		Average...	1·37

of gases. For its evaluation the formula for viscosity was used which Chapman, and independently of him Enskog, has deduced. This formula accounts for intermolecular

forces and gives also collisional diameters. But they correspond to a temperature much higher than the diameters calculated by (6). According to that the values for s^* are smaller than the values for s in the average about 30 per cent.

The molecule being identical with the atom in the case of argon, we may compare its value for s with the value for the atomic diameter which is calculated by the formula of Eucken-Lindemann †, giving a collisional diameter corresponding to the melting-point. Assuming that the crystalline argon has a face-centred cubic lattice as proved from X-ray measurement by Simon and v. Simson ‡, we obtain for the diameter $3{\cdot}6 \times 10^{-8}$ cm. in perfect accordance with the value from (6). The corresponding temperatures are practically identical, the melting-point being 85° K and the boiling-point to which (6) relates 87° K.

Institut f. theoretische Physik
an der Universität, Vienna.
Jan. 20, 1925.

Yours faithfully,
H. Sirk.

LXXV. *Variation of Logarithmic Decrement with Amplitude and Viscosities of certain Metals.* *By* G. Subrahmaniam, *M.A., A.Inst.P., and* D. Gunnaiya, *M.A., A.Inst.P.*§

Introduction.

With a view to determine the absolute coefficient of viscosity of certain liquids by oscillating a solid of "easy" shape, the authors have used a fine copper wire as suspension and have noticed remarkable variation of logarithmic decrement with amplitude. The results are not quite in agreement with those obtained by others, and could not therefore be represented by any one of the empirical formulæ proposed. They have therefore instituted a series of experiments to study, at some length, the nature of variation of logarithmic decrement with amplitude and, if possible, to correlate it with other elastic properties of the material. The results obtained seem of sufficient general interest to merit publication, and the authors therefore propose to set

† Eucken, *Grundriss der physikalischen Chemie*, p. 342.
‡ *Zeitschr. f. Physik*, xxv. p. 160 (1924).
§ Communicated by Prof. E. H. Barton, F.R.S.

forward the results of their experiments, in the first instance, with copper, brass, and steel wires.

The change of both the logarithmic decrement and the period with amplitude has, of course, long been recognized. Schmidt * and, later on, Voigt † have found that the logarithmic decrement varies approximately as the square of the amplitude, while Streintz ‡ found it to be independent of the amplitude in torsional vibrations and also of the period. Guthe and Sieg §, experimenting with certain platinum iridium wires, found that the decrement amplitude curves show a maximum value, and that this value depends on the initial amplitude. Harris ‖, on the other hand, using bismuth wires, observed a decrease of the logarithmic decrement with decreasing amplitude, but no maximum or minimum values. George A. Lindsay¶ concluded that the decrement of longitudinal vibrations of wires made of copper is proportional to the amplitude, and that the increase for other metals is less regular.

Such behaviour of wires is influenced to a marked extent by (i.) internal friction and (ii.) elastic fatigue or after-effect; and accordingly either or both of these causes is supposed to account for the observed differences in the rates of subsidence of vibrations. If the damping is caused by the elastic after-effect, the logarithmic decrement, according to Boltzmann's theory, is independent of the period; and if there is really internal friction, the decrement depends on the period. The results of Voigt's** work were not entirely in favour of either theory, and his conclusion was that in some cases the preponderant factor in damping is internal friction, in other cases it is the after-effect.

The viscous resistances called into play when a wire is set in vibration and to which the decay is largely due do not seem to be of the ordinary type; that is to say, such as are proportional to the rates of strain. If this type of resistance alone were involved, the proportionate diminution of the amplitude of oscillations per unit of time, as Lord Kelvin††

* Wied, *Ann.* ii. p. 48 (1877).

† *Abh. der Konigl. Gesell. der Wiss. zu Göttingen*, xxxviii. p. 189.

‡ *Wien. Ber.* lxix., II. Abt. p. 337 (1874); lxxx., II. Abt. p. 397 (1879).

§ Phys. Rev. xxx. no. 4 (1910).

‖ Phys. Rev. xxxvi. no. 2 (1912).

¶ Phys. Rev. June 1914.

** *Loc. cit.*

†† 'Mathematical and Physical Papers,' iii. p. 27.

pointed out, would be inversely proportional to the square of the period.

Besides these two chief causes, the dissipation of energy from the point of suspension * outwards also, perhaps, partly accounts for the variation of decrement with amplitude.

Experiments.

On the present occasion wires made of three different materials—namely, copper, brass, and steel—are used. In each case experiments are conducted with wires of different thicknesses and of different lengths. In view of the large amount of attention which the study of elastic properties of copper wires received at the hands of Lord Kelvin †, Joseph O. Thomson ‡, and several others, it is thought desirable to experiment with a greater number of wires made of copper than of the remaining two. These copper and brass wires are taken from ordinary commercial spools supplied by an electric warehouse, and are therefore of doubtful composition ; the steel wires are, however, the best piano wires from Misquith and Co.

Each of these wires before it is experimented on is kept stretched by half the maximum load which it can carry for the given dimensions, and is allowed to remain in that condition for several days. The wire is then suspended in an air-free chamber to the top of a massive stand by means of a self-centering three-jawed chuck, the lower end being fixed to a rotating cylinder by a similar device. Before readings are taken it is found necessary to bring the wires to a steady state. In the initial stages no two consecutive sets of readings agreed closely, so that the wires were kept in a state of continuous vibration for, indeed, a pretty long time before perfect consistency could be achieved. Thus in the case of the thinnest copper wire the values for the logarithmic decrement for a *given amplitude* progressively diminished with each successive trial, until at last it tended to a constant value. The time for which these wires should be kept thus continuously vibrating before constancy is obtained is, however, different for different metals, and even for the same metal it is found to increase with cross-section.

* Kôtarô Honda and Seibi Konno, Phil. Mag. July 1921 : and Iokibe, Phil. Mag. Sept. 1921.

† *Loc. cit.*

‡ Phys. Rev. March 1899.

For copper this interval is about three to five hours, for brass about six to ten hours, whereas for steel it is as great as five to seven days.

A small bit of mirror is attached to the wire immediately above the lower chuck, and the wire in addition carries a fine pointer bent vertically down at the back of the mirror. The successive amplitudes are read off by the usual telescope and scale method, and for appreciable values this method, though simple, is found to answer exceeedingly well, as a sufficiently quick and trained eye can read correctly to a tenth of a millimetre. When the extent of the swing has fallen to about a centimetre the following method is adopted. A telemicroscope having in its eyepiece a scale divided into tenths of a millimetre is focussed on the vertical pointer behind the mirror, and is permanently arranged on the other side of the telescope and scale. The extent of the swing of the pointer is read off on the scale within the eyepiece. Readings so obtained are correct to a hundredth of a millimetre, as will be seen from the experimental results tabulated below.

One peculiarity which the authors have noticed in the course of these experiments deserves special mention, though it may be a repetition * of what others engaged in similar work have observed. For a particular length of one of the copper wires the amplitude is found to diminish gradually, and after a time, strangely enough, the values increase, and this progressive rise and fall is quite periodical and lasts for a considerable length of time. At the same time it is observed that the torsional pendulum begins to make pendulous oscillations, though, to start with, the vibrations are purely torsional. These pendulous oscillations are again noticed to die down, to be reborn again, and so on. This anomalous behaviour is evidently due to the mutual transference of energy from torsional to pendulous oscillations and *vice versa*, and arises from the synchronization of the two periods—a fact so conspicuous in the theory of resonance.

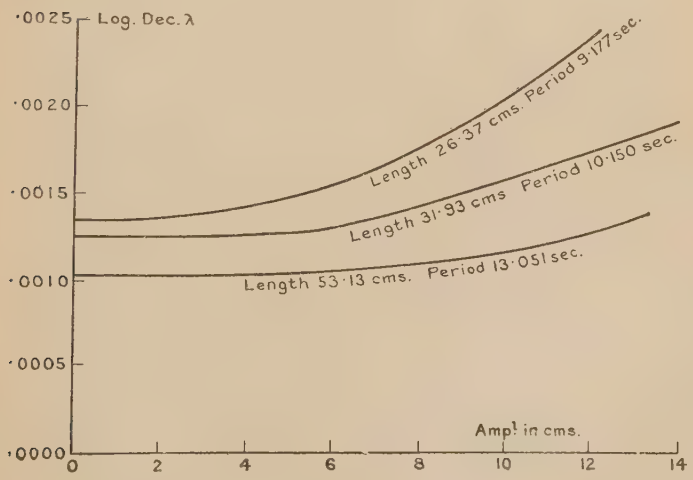
* Herbert Tomlinson, Proc. Phys. Soc. August 1886.

Experimental Results.

Copper Wire, diam. 0·03302 cm. (Graph No. 1.)

Length, 53·13 cm. Period, 13·051 sec.		Length, 31·93 cm. Period, 10·15 sec.		Length, 26·37 cm. Period, 9·177 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
13·20	0·001394	14·00	0·001901		
12·37	1321	12·81	1808		
11·01	1238	11·62	1701	11·40	0·002334
9·80	1171	10·50	1669	10·23	2129
8·30	1109	9·63	1554	9·27	1915
7·54	1094	8·87	1501	8·58	1871
6·80	1082	7·58	1411	7·82	1750
6·13	1071	6·60	1335	6·43	1582
5·50	1062	5·95	1305	5·60	1529
4·86	1051	5·13	1284	5·03	1490
4·15	1049	4·24	1272	4·75	1471
3·64	1045	3·80	1261	4·12	1436
3·20	1047	3·02	1257	3·84	1417
2·90	1043	2·45	1253	3·23	1386
2·20	1045	2·00	1250	2·42	1361
1·45	1042	1·63	1249	1·95	1353
1·00	1046	1·21	1251	1·50	1350
·812	1049	·771	1253	·778	1352
·631	1045	·603	1248	·601	1349
·504	1044	·382	1251	·417	1348
·235	1043	·219	1251	·239	1348

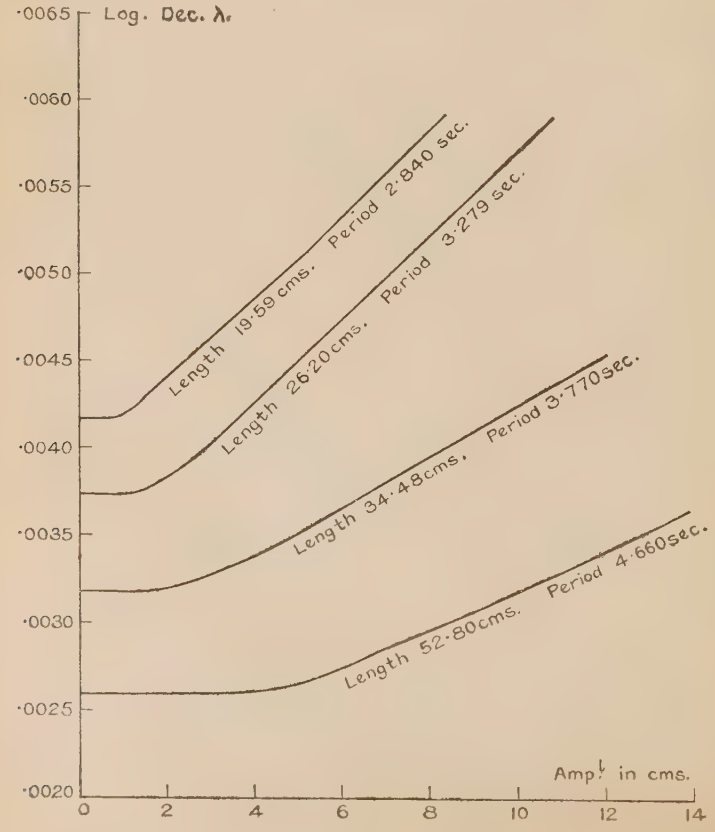
Graph 1.



Copper Wire, diam. 0·0555 cm. (Graph No. 2.)

Length, 52·8 cm. Period, 4·66 sec.		Length, 34·5 cm. Period, 3·77 sec.		Length, 26·2 cm. Period, 3·28 sec.		Length, 19·6 cm. Period, 2·84 sec	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec
15·10	0·003710						
13·23	3508	12·09	0·004551				
11·72	3350	11·02	4408	11·21	0·005982		
9·80	3142	9·83	4245	10·13	5709		
8·48	2996	8·51	4052	9·40	5501		
7·10	2874	7·20	3860	8·60	5364	8·52	0·005936
6·30	2802	6·41	3748	7·82	5204	7·30	5658
5·12	2694	5·41	3600	6·56	4904	6·32	5426
4·78	2670	4·87	3532	5·71	4710	5·12	5143
3·65	2637	3·64	3388	5·12	4560	4·40	4977
3·15	2620	3·00	3312	4·30	4358	3·48	4746
2·80	2616	2·13	3250	3·47	4169	2·50	4524
2·50	2614	1·60	3231	2·91	4048	2·13	4431
2·18	2614	1·12	3210	2·63	3984	1·62	4314
1·70	2615	·83	3204	2·30	3910	1·19	4224
1·30	2610	·61	3170	1·91	3859	·90	4220
1·02	2614	·38	3202	1·50	3808	·75	4200
·80	2615	·31	3201	1·13	3771	·62	4197
·62	2614	·20	3202	·82	3760	·50	4196
·53	2614			·55	3760	·38	4191
·35	2613			·52	3758	·23	4196
·28	2610			·33	3764		

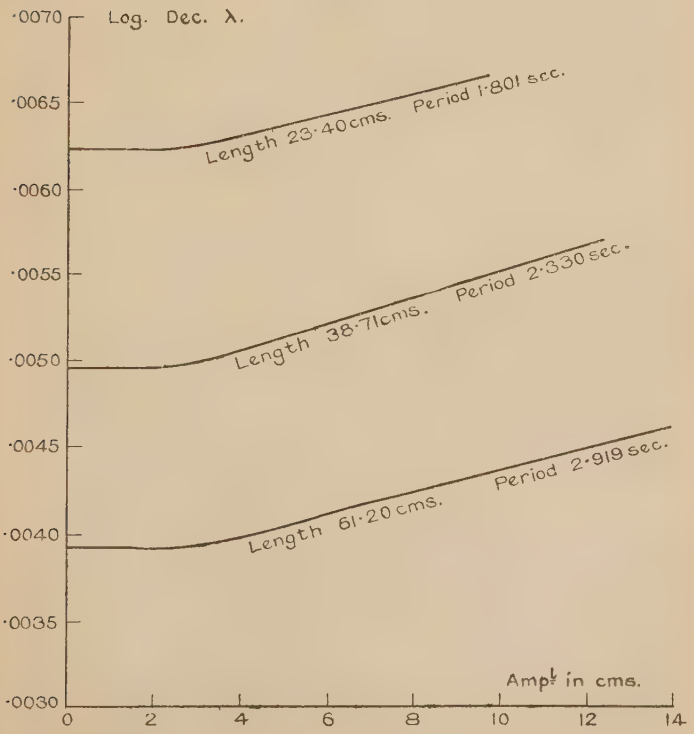
Graph 2.



Copper Wire, diam. 0·0730 cm. (Graph No. 3.)

Length, 61·20 cm. Period, 2·92 sec.		Length, 38·70 cm. Period, 2·33 sec.		Length, 23·40 cm. Period, 1·80 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
13·81	0·004590	13·20	0·005746		
12·03	4484	11·81	5644		
11·50	4448	10·29	5532		
9·62	4334	9·12	5441	9·61	0·006647
8·40	4250	8·31	5374	8·30	6566
7·50	4198	7·20	5292	7·78	6537
6·17	4110	6·45	5250	7·12	6500
5·02	4048	5·50	5165	6·50	6460
4·10	3999	4·60	5100	5·31	6384
3·20	3963	4·12	5064	4·20	6320
2·81	3945	3·81	5049	3·50	6280
2·42	3941	3·20	5005	2·70	6256
1·90	3935	2·50	4962	2·18	6249
1·40	3934	2·03	4959	1·80	6246
1·01	3936	1·80	4956	1·41	6244
·831	3940	1·40	4955	·91	6245
·642	3934	1·06	4956	·71	6246
·482	3936	·818	4955	·50	6245
·301	3935	·603	4960	·28	6249
		·504	4954		
		·286	4956		

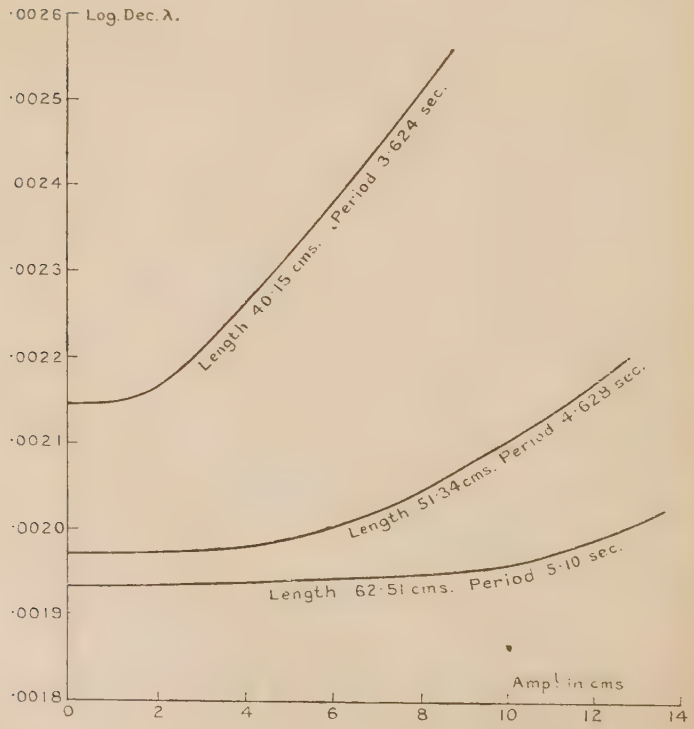
Graph 3.



Brass Wire, diam. 0·05750 cm. (Graph No. 4.)

Length, 62·50 cm. Period, 5·10 sec.		Length, 51·34 cm. Period, 4·628 sec.		Length, 40·15 cm. Period, 3·624 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Loc. dec.
13·50	0·002019				
12·12	1996	12·94	0 002201		
11·05	1978	11·89	2165		
10·20	1967	10·23	2106		
9·41	1959	9·40	2084		
8·73	1954	8·71	2066	8·40	0·002534
7·59	1948	7·52	2037	7·52	2474
6·23	1944	6·95	2024	6·83	2430
5·88	1942	6·00	2009	5·90	2371
5·17	1940	5·24	1997	5·01	2320
4·40	1938	4·38	1983	4·33	2281
3·90	1937	3·40	1979	3·80	2249
3·12	1935	2·89	1974	3·12	2211
2·39	1934	2·10	1972	2·80	2198
1·45	1932	1·51	1971	2·20	2169
1·00	1933	·942	1971	1·79	2158
·810	1934	·729	1970	1·24	2151
·709	1931	·602	1969	·972	2148
·602	1931	·408	1971	·799	2146
·430	1934	·283	1970	·621	2146
·291	1932			·482	2147
				·312	2144

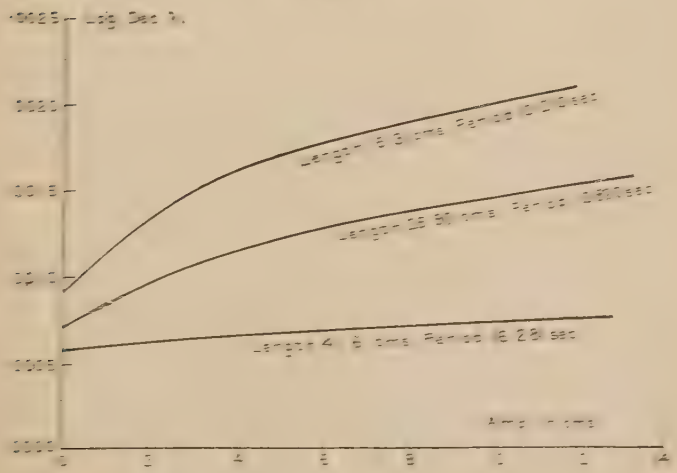
Graph 4.



Steel Piano Wire, diam. (=)2350 cm. (Graph No. 5.)

Length, 4180 cm. Period, 1·028 sec.		Length, 2740 cm. Period, 1·282 sec.		Length, 1630 cm. Period, 1·021 sec.	
Ampl. cm.	Log. Dec.	Ampl. cm.	Log. Dec.	Ampl. cm.	Log. Dec.
12·00	0·0007715	8·30	0·0010420		
10·87	7182	7·80	1060	11·20	0·0003044
9·87	7312	7·12	1472	10·10	3026
7·75	7318	6·24	1387	8·72	1946
6·72	7360	5·40	1325	7·15	1951
5·85	8010	4·64	1294	6·20	1745
5·12	8022	3·98	1233	5·41	1729
4·57	8732	3·51	1190	4·75	1685
4·06	8961	3·01	1179	4·20	1668
3·66	9042	2·62	1125	3·71	1704
3·34	9004	2·31	1104	3·24	1696
2·90	9810	2·01	1081	2·83	1478
2·57	9842	1·82	1045	2·49	1522
2·31	1·0267	1·58	1025	2·01	1540
1·82	0·9892	1·35	1002	1·82	1309
1·61	0·9795	1·16	0981	1·57	1349
1·41	0·9812	1·01	0942	1·11	1164
1·20	0·9820	0·89	0920	0·981	1125
1·09	0·9902	0·78	0873	0·902	1061
1·16	0·9851	0·68	0847	0·74	1055
0·824	0·9922	0·60	0827	0·67	1045
0·714	0·9951	0·52	0821	0·593	1011
0·62	1·0001	0·46	0870		

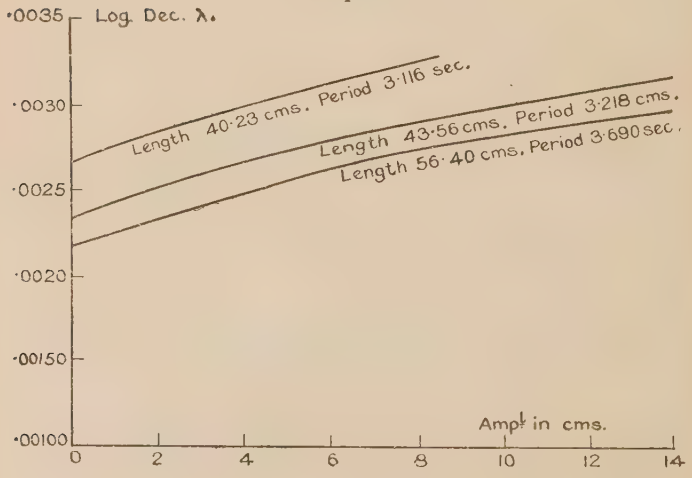
Graph 5.



Steel Piano Wire, diam. 0·05350 cm. (Graph No. 6.)

Length, 56·40 cm. Period, 3·69 sec.		Length, 43·56 cm. Period, 3·22 sec.		Length, 40·23 cm. Period, 3·12 sec.	
Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.	Ampl. cm.	Log. dec.
11·84	0·002889	13·50	0·003139		
9·60	2789	12·33	3092		
8·58	2754	11·49	3060		
7·40	2696	10·72	3019		
6·40	2642	9·80	2987		
5·22	2560	8·34	2914	8·41	0·003287
4·88	2460	7·40	2866	7·59	3210
3·75	2451	6·51	2820	6·49	3143
3·25	2400	5·72	2771	5·98	3110
2·92	2378	5·03	2725	5·10	3051
2·60	2352	4·42	2688	4·32	2999
2·28	2330	3·80	2641	3·51	2940
1·80	2296	3·01	2588	2·20	2834
1·40	2261	2·68	2563	1·70	2796
1·12	2239	2·10	2514	1·21	2756
·911	2226	1·70	2479	·852	2730
·613	2203	1·21	2430	·771	2721
·524	2192	·905	2401	·543	2703
·341	2173	·682	2384	·390	2693
·250	2169	·509	2365	·257	2679
		·392	2353	·211	2674
		·272	2340		

Graph 6.



A Study of the Results.

These values are plotted on graph paper, amplitudes in cm. being marked along the x-axis and logarithmic decrements along the y-axis. In all these experiments the scale is held at a constant distance of 74 cm., so that an amplitude of 1 cm. corresponds to a twist of $\frac{1}{74\times 2}\times\frac{180}{\pi}$ $=0{\cdot}39$ of a degree. Since in no case did the amplitude exceed about 14 cm., the maximum twist to which the wires were subjected never exceeded about 4·86 degrees.

The nature of the resulting curves is indeed very suggestive, and seems to be characteristic of the particular material. With copper wires the decrement seems to be approximately constant for amplitudes *below a certain limiting value*, and then to vary linearly with it. This is the characteristic feature of one and all of the copper wires examined, and the curves suggest an equation of the form

$$\lambda_a=\lambda_0+f(a-m),$$

where λ_a is the decrement for amplitude "a," λ_0 that when the amplitude is zero, "m" the limiting amplitude, and $f(a-m)$ a linear function. For all values of "a" less than or equal to "m," $f(a-m)=0$, so that $\lambda_a=\lambda_0$.

The value of "m" depends both on the cross-section and on the length of the wire. Owing to the dissipation of energy, the minimum decrement for a given cross-section does not correspond to the same twist per unit length of the wire. Thus, for the thinnest wire (diam. ·03302 cm.) the decrement reaches a constant value when the twist per unit length is 1·85, 1·98, and 2·13 minutes (of arc) when the lengths of the wires are 53·13, 31·93, and 26·37 cm. respectively. With the second copper wire (diam. ·0555 cm.) the constant value is reached for twists (per unit length) of 1·21, 1·02, 1·14, and 1·23 minutes when the lengths are 52·8, 34·5, 26·2, and 19·6 cm. respectively; and with the third wire (diam. ·0730 cm.) the constant value is reached for twists (per unit length) of 1·15, 1·51, and 1·84 minutes when the lengths are 61·2, 38·7, and 23·4 cm. respectively.

With wires of very narrow cross-section the curves get steeper and steeper for decreasing lengths. As the thickness of the wires is increased, it is, however, seen that they tend more and more towards parallelism. Of wires of the same material, those that are thinner appear to be steeper than those of greater cross-section.

The behaviour of brass wires is quite similar to that of copper. The logarithmic decrement remains constant over a certain range, and increases linearly thereafter. When the twists per unit length are 1·08, 1·11, and ·96 of a minute respectively, this constant value seems to have been reached. Both in the case of copper and in that of brass, as the bend of the curves is rather ill-defined, these values of twists per unit length are at best approximate. For thicker wires, however, the bend is relatively well-defined, as can be seen from the curves for copper.

The curves for steel wires, on the other hand, present features quite distinct from those of either copper or brass. The decrement does not tend to a constant value, but decreases with decreasing amplitude, more or less linearly, so that $\lambda_a=\lambda_0+f(a)$ where $f(a)$ is a linear function. Owing to the bend of the curves, which is more pronounced with narrower than with thicker wires, the nature of this function is different according as the curve is taken before or after the bend. For wires of diameter ·02350 cm. the curves become steeper for shorter lengths, whereas with thicker steel wires they tend more towards parallelism. In the latter case the bend is less marked and the curves approximate to right lines.

Viscosities of Metals.

The equation of motion for the torsional oscillations is

$$\mathrm{I}.\frac{d^2\theta}{dt^2}+b.\frac{d\theta}{dt}+c\theta=0,$$

where b and c are the damping and restoring coefficients respectively. $c=\frac{\pi.n.\mathrm{R}^4}{2l}$, where n is the rigidity modulus, and b, as shown by Honda (*loc. cit.*), is $\frac{\pi.\eta.\mathrm{R}^4}{2l}$, where η is the coefficient of viscosity. The equation thus finally becomes

$$\mathrm{I}.\frac{d^2\theta}{dt^2}+\frac{\pi.\eta.\mathrm{R}^4}{2l}.\frac{d\theta}{dt}+\frac{\pi.n.\mathrm{R}^4}{2l}.\theta=0,$$

the solution of which is

$$\theta=\theta_0.e^{-\frac{\pi.\eta.\mathrm{R}^4}{2l}.\frac{t}{2\mathrm{I}}}\left(\frac{2\pi t}{\mathrm{T}}+\epsilon\right).$$

The logarithmic decrement is thus

$$\lambda = \frac{\pi \,.\, \eta \,.\, R^4 T}{8Il};$$

$$\therefore \quad \eta = \frac{8 \,.\, Il\lambda}{\pi R^4 T}.$$

In the following tabular form the viscosities are calculated, taking the minimum values of λ :—

I, 3840·9 grm. cm.^{2} Temperature, 27°·5–29°·7 C.

Material.	R.	l.	T.	Log. dec.	$\lambda = \frac{8Il\lambda}{\pi R^4 T} \times 10$	
	cm.	cm.	sec.	λ.	dynes per sq. cm.	
Copper	·01651	53·13	13·051	0·001046	5·610	mean 5·30
,, ...	,,	31·93	10·150	1250	5·182	
,, ...	,,	26·37	9·177	1349	5·103	
,, ...	·02775	52·80	4·66	2614	4·888	mean 4·89
,, ...	,,	34·50	3·77	3202	4·885	
,, ...	,,	26·20	3·28	3760	4·955	
,, ...	,,	19·60	2·84	4191	4·722	
,, ...	·03650	61·20	2·92	3935	4·550	mean 4·52
,, ...	,,	38·70	2·33	4956	4·480	
,, ...	,,	23·40	1·80	6245	4·540	
Brass	·02875	62·50	5·10	1933	3·393	mean 3·31
,, ...	,,	51·34	4·628	1970	3·129	
,, ...	,,	40·15	3·624	2146	3·404	
Steel	·01175	41·6	16·281	0582	7·635	mean 7·57
,, ...	,,	25·9	12·821	0721	7·483	
,, ...	,,	16·3	10·210	0928	7·601	
,, ...	0·02675	56·4	3·690	2158	6·31	mean 6·30
,, ...	,,	43·56	3·218	2326	6·02	
,, ...	,,	40·23	3·116	2665	6·58	

η for a given material, though fairly constant when the cross-section is the same, appears to fall off as thickness is increased. This is true of both copper and steel.

Summary and Conclusions.

(1) The logarithmic decrement is not constant for different amplitudes, but is found to vary appreciably.

(2) In the case of copper and brass wires the decrement remains constant over a certain range, depending on the material, its length, and cross-section, and then varies linearly.

(3) The behaviour of steel wires is quite different. The decrement does not show any constant value, but falls off steadily with decreasing amplitudes.

(4) The viscosities of three different specimens of copper wire are found to be $4{\cdot}52 \times 10^8$, $4{\cdot}89 \times 10^8$, and $5{\cdot}30 \times 10^8$ dynes per sq. cm. ; that of brass $3{\cdot}31 \times 10^8$ dynes per sq. cm. ; and that of two specimens of steel wires $7{\cdot}57 \times 10^8$ and $6{\cdot}30 \times 10^8$ dynes per sq. cm. These discrepancies are perhaps due to varying impurities in the case of copper and to varying composition in the case of steels.

In conclusion, the authors wish to thank Prof. A. L. Narayan, M.A., D.Sc., F.Inst.P., under whose guidance the present investigation was carried out.

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LXXVI. *Internal Friction as a Cause of Shaft Whirling.* *By* A. L. Kimball, Jr. *.

MANY articles have been written upon causes of the whirling of shafts, but, so far as the writer is aware, it is only within the last year that internal friction within the shaft, or within the rotor itself, has been suggested as a cause of whirling †.

It might be supposed, at first thought, that internal friction would damp out whirling. In this paper it will be shown that under the right conditions internal friction will sustain a whirl rather than damp it out.

Consider, for example, a shaft deflected as shown in fig. 1. Fig. 1 *a* shows a top view of a cross-section of the same shaft. Owing to its deflexion, all the fibres in the right-hand half of its cross-section are in tension T_e, and all of the fibres in the left-hand half are in compression C_e. On tending to straighten itself, the shaft reacts from right to left, or from the tension side T_e to the compression side C_e. This reaction is represented by the force vector R_e.

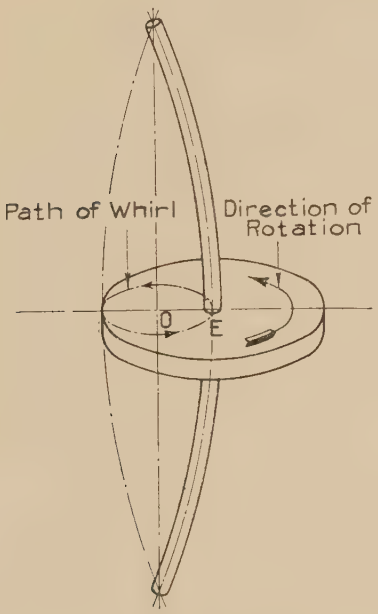
If internal friction exists, however, every fibre is also subject to a force due to internal friction. These internal friction forces do not depend upon the length of the fibres, but only come into play when the length of the fibres *is being changed*, such as the force resulting from the stretching of a

* Communicated by the Author.

† A. L. Kimball, Jr., Phys. Review, xxi. p. 703 (June 1923). B. L. Newkirk, G. E. Review, xxvii. p. 169 (March 1924). A. L. Kimball, Jr., G. E. Review, xxvii. p. 244 (April 1924).

fibre of molasses candy. When a fibre is being stretched, internal friction will evidently produce a tension; when a fibre is being compressed a compression is produced. If the shaft is revolving in a counter-clockwise direction, as indicated in fig. 1 *a*, all fibres in the lower half of the cross-section are being stretched, and are thus under frictional tension T_f, and all fibres in the upper half are being compressed, and consequently are under frictional compression C_f. Just as the *elastic* tensions and compressions on the fibres produce a reaction to the left from T_e to C_e, so also the

Fig. 1.



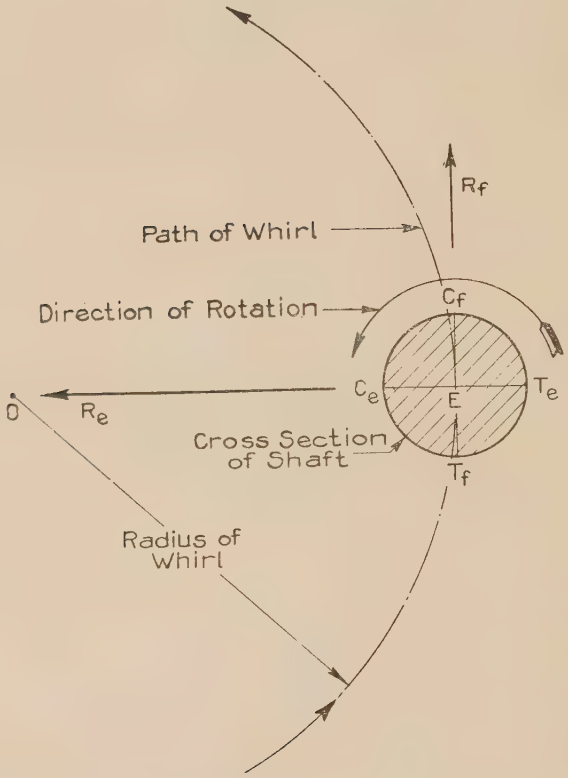
frictional tensions and compressions produce a reaction upwards, in the figure, from T_f to C_f. This reaction is represented by the vector R_f.

The elastic reaction R_e may be very powerful, and will quickly disappear unless maintained by centrifugal force when the entire shaft and fly-wheel are "whirling" at or very close to the critical resonant speed. The frictional reaction R_f, although far smaller than R_e, is seen to be unbalanced, so that as long as R_f is in the same direction as the whirl, as shown in fig. 1, the whirl must continually

build up until frictional resistance is produced sufficient to balance the disturbing force R_f.

The disturbing force R_f is in the same direction as the whirling motion in the case cited, so that whirling builds up. A further consideration of fig. 1 *a* shows that this is only true when the shaft rotates about E faster than the plane of

Fig. 1 *a*.



deflexion of the shaft revolves about O, otherwise the fibres shown in the upper half of the cross-section given in the figure will be increasing instead of decreasing in length, and those below will be decreasing instead of increasing in length, causing the reaction R_f due to frictional forces to reverse, and to act against the motion of the shaft in its path of whirl instead of with this motion. Whirling will be damped out instead of sustained, due to this cause when the

shaft is revolving more slowly than its natural whirling speed.

In order to build up a whirl from internal friction action, therefore, a shaft must revolve with a higher speed than its whirling speed. Furthermore, it is seen that, due to internal friction, a shaft may whirl when running at any speed of revolution above its critical speed. The whirling itself must be at or near the critical speed. A whirl at any other speed is dynamically impossible without a powerful disturbing force, just as the vibration of a reed at any other than its natural frequency is impossible without a strong stimulus.

Fortunately, in steel such as is used for ordinary shafting the internal friction is so small that a whirl, due to this cause, will not develop unless the conditions are exactly right. For example, if the bearings are not rigidly supported, the energy loss because of their vibration may completely annul the effect.

It has been discovered that this internal friction action may be greatly increased if a shaft has external parts such as rings shrunk on to it. In such a case a whirl is very difficult to avoid. The disturbing force R_f (fig. 1 *a*) is caused just as before, except that the friction comes largely from the rubbing of the surface fibres of the shaft against the inner surface of the ring, which is shrunk on to the shaft. This surface friction may be so great as to cause a shaft to take a slight permanent set when given a small deflexion. Under these conditions a whirl is almost certain to develop when the rotational speed rises above the critical speed.

This cause of whirling was discovered in connexion with a peculiar whirling or whipping developed by large turbo compressors built by the General Electric Company of America *, and has been overcome chiefly by the use of spring bearings producing an absorption of vibrational energy.

In this article no assumptions are made as to what laws the internal frictional force obeys, as they are not well understood. The important fact is that this disturbing force must exist if internal friction is present, and that the force may produce whirling.

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July 25, 1924.

* B. L. Newkirk, Gen. Elec. Review, xxvii. p. 169 (March 1924).

LXXVII. *A Class of equivalent Electrical Networks.* By The Research Staff of the General Electric Co., Ltd.* (*Work conducted by* A. C. Bartlett.)

Summary.

Firstly, it is shown that there exists a large number of alternative networks that have the same impedance as networks made up of numbers of T, Π, or Bridge artificial line sections short-circuited or open-circuited at the far end.

Secondly, by the use of these networks a single Bridge type section can be made in a large number of ways that is equivalent, both as regards input and output terminals, to an artificial line consisting of any number of equal sections.

A Class of equivalent Electrical Networks.

IN telephone engineering use is often made of artificial lines composed of a number of similar sections, each section having two input terminals and two output terminals,

Fig. 1.

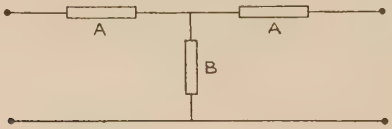
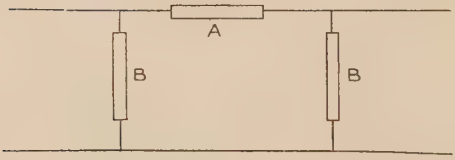


Fig. 2.

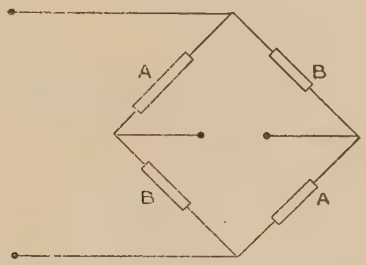


the input terminals of any section being connected to the output terminals of the previous section. The most common sections are the T, Π, and Bridge sections shown in figs. 1, 2, and 3, the impedance elements A & B being each composed

* Communicated by the Director.

of some arrangement of resistances, condensers, and inductances. Electric wave filters are a special case in which A & B are pure reactances.

Fig. 3.



The general transmission theory of such networks is identical with that of the uniform line except that n, the number of sections, replaces l the length of the uniform line.

Whichever form of section is employed the impedance of n sections is $Z_0 \tanh n\theta$ if the network is short-circuited at the far end, and $Z_0 \coth n\theta$ if it is open at the far end, where Z_0 is the characteristic impedance, and θ the propagation constant of a single section. The relations between Z_0 and θ for the different sections are given below.

T section.

$$Z_0 = \sqrt{A^2 + 2AB},$$

$$Z_0 \tanh \frac{\theta}{2} = A,$$

$$Z_0 / \sinh \theta = B,$$

$$Z_0 \coth \frac{\theta}{2} = A + 2B,$$

$$Z_0 \tanh \theta = A + \frac{AB}{A+B},$$

$$Z_0 \coth \theta = A + B.$$

Π section.

$$Z_0 = \frac{AB}{\sqrt{A^2+2AB}},$$

$$Z_0 \sinh\theta = A,$$

$$Z_0 \coth\frac{\theta}{2} = B,$$

$$Z_0 \tanh\frac{\theta}{2} = \frac{1}{\frac{1}{B}+\frac{2}{A}} = \frac{A^2B}{A^2+2AB},$$

$$Z_0 \tanh\theta = \frac{1}{\frac{1}{B}+\frac{1}{A}} = \frac{AB}{A+B},$$

$$Z_0 \coth\theta = \frac{1}{\frac{1}{B}+\frac{1}{A+B}} = \frac{B(A+B)}{A+2B}.$$

Bridge section.

$$Z_0 = \sqrt{AB},$$

$$Z_0 \coth\frac{\theta}{2} = A \text{ or } B,$$

$$Z_0 \tanh\frac{\theta}{2} = B \text{ or } A.$$

Of course only two equations are independent in each case ; the reason for giving more than two will appear later. In this paper it will be shown firstly, that there is a large number of networks that have the same impedance at all frequencies as an artificial line consisting of any number of either similar T, Π, or Bridge sections open or short circuited at the far end ; and secondly, that a single Bridge type section can be constructed that is equivalent at all frequencies, both as regards input and output terminals, to an artificial line consisting of any number of either T, Π, or Bridge sections.

Considering the first part of the problem. Any expansion of Z tanh $n\theta$ or Z coth $n\theta$ in terms of simpler functions, such as $Z_0 \tanh\theta$, $Z_0 \coth\theta$, or $Z_0 \sinh\theta$, that represents the impedance of a network built up of the simple networks represented by these functions will give a network whose impedance is $Z_0 \tanh n\theta$ or $Z_0 \coth n\theta$.

Examination of hyperbolic identities show that a large number exist that fulfil these conditions.

Among the most important are :—

$$\text{Tanh } n\theta = \frac{n \tanh \theta}{1+} \frac{(n^2-1^2)\tanh^2\theta}{3+} \frac{(n^2-2^2)\tanh^2\theta}{5+} \cdots,$$

$$\text{Tanh } n\theta = \sum_{r=0}^{r=\frac{n}{2}-1} \frac{\tanh\theta \cdot \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n} \cdot \pi}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{2r+1}{2n} \cdot \pi}}$$

when n is even,

$$\text{Tanh } n\theta = \frac{\tanh\theta}{n} + \sum_{r=0}^{r=\frac{n-3}{2}} \frac{\tanh\theta \cdot \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n} \cdot \pi}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{2r+1}{2n} \cdot \pi}}$$

when n is odd,

$$\text{Coth } n\theta = \frac{1}{n}(\tanh\theta + \coth\theta) + \sum_{r=1}^{r=\frac{n}{2}-1} \frac{\tanh\theta \cdot \dfrac{2}{n \sin^2 \dfrac{r\pi}{n}}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{r\pi}{n}}}$$

when n is even,

$$\text{Coth } n\theta = \frac{\coth\theta}{n} + \sum_{r=1}^{r=\frac{n-1}{2}} \frac{\tanh\theta \cdot \dfrac{2}{n \sin^2 \dfrac{r\pi}{n}}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{r\pi}{n}}}$$

when n is odd,

$$\text{Tanh } \frac{n\theta}{2} = \frac{1}{n} \sum_{r=0}^{r=\frac{n}{2}-1} \frac{1}{\dfrac{\sin^2 \dfrac{2r+1}{2n} \cdot \pi}{\sinh\theta} + \frac{1}{2}\tanh\dfrac{\theta}{2}}$$

when n is even,

$$\operatorname{Coth}\frac{n\theta}{2}=\frac{1}{n}\left\{2\coth\theta+\sum_{r=1}^{r=\frac{n}{2}-1}\frac{1}{\dfrac{\sin^2\dfrac{r\pi}{n}}{\sinh\theta}+\frac{1}{2}\tanh\frac{\theta}{2}}\right\}$$

when n is even.

$$\operatorname{Tanh}\frac{n\theta}{2}=\frac{1}{n}\left\{\tanh\frac{\theta}{2}+\sum_{r=0}^{r=\frac{n-3}{2}}\frac{1}{\dfrac{\sin^2\dfrac{2r+1}{2n}.\pi}{\sinh\theta}+\frac{1}{2}\tanh\frac{\theta}{2}}\right\}$$

when n is odd,

$$\operatorname{Coth}\frac{n\theta}{2}=\frac{1}{n}\left\{\coth\frac{\theta}{2}+\sum_{r=1}^{r=\frac{n-1}{2}}\frac{1}{\dfrac{\sin^2\dfrac{r\pi}{n}}{\sinh\theta}+\frac{1}{2}\tanh\frac{\theta}{2}}\right\}$$

when n is odd.

First, consider the identity

$$\tanh n\theta=\frac{n\tanh\theta}{1+}\,\frac{(n^2-1^2)\tanh^2\theta}{3+}\,\frac{(n^2-2^2)\tanh^2\theta}{5+}\cdots$$

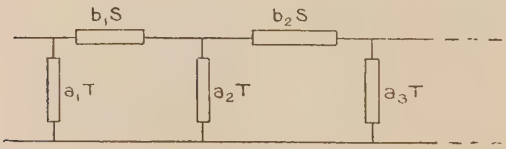
From this we obtain

$$Z_0\tanh n\theta=\frac{1}{1/nZ_0\tanh\theta+}\,\frac{1}{\dfrac{3n}{n^2-1^2}.Z_0\coth\theta+}$$

$$\frac{1}{1\Big/\dfrac{n(n^2-2^2)}{5(n^2-1^2)}.Z_0\tanh\theta+}\cdots$$

But this is the impedance of the network of fig. 4:

Fig. 4.



where $S = Z_0 \coth \theta$,

$T = Z_0 \tanh \theta$,

$$a_1 = n, \qquad b_1 = \frac{3n}{n^2-1},$$

$$a_2 = \frac{n(n^2-2^2)}{5(n^2-1)}, \qquad b_2 = \frac{7n(n^2-2^2)}{(n^2-1)(n^2-3^2)}$$

$$a_3 = \frac{n(n^2-2^2)(n^2-4^2)}{9(n^2-1^2)(n^2-3^2)}, \qquad b_3 = \frac{11n(n^2-2^2)(n^2-4^2)}{(n^2-1)(n^2-3^2)(n^2-5^2)}.$$

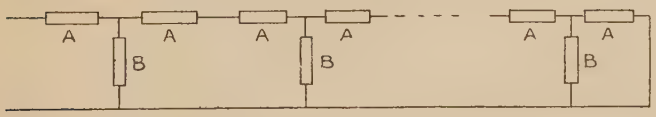
Consider for example the T section artificial line :

$$Z_0 \coth \theta = A + B.$$

$$Z_0 \tanh \theta = A + \frac{AB}{A+B} = A + \frac{1}{\frac{1}{A}+\frac{1}{B}}.$$

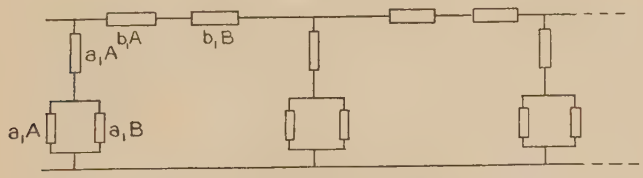
Then $Z_0 \tanh n\theta$, which is the impedance of the network of fig. 5 having n sections, and short-circuited at the far end,

Fig. 5.



is by the above result shown to be also the impedance of the network of fig. 6.

Fig. 6.



A like result for $Z_0 \coth n\theta$ can be obtained from the same expansion of $\tanh n\theta$ but can be written down directly by means of the Method of Reciprocal Impedances, which may be regarded as a special case of the Principle of Duality *

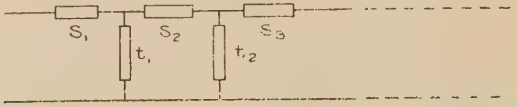
* Russell, ' Alternating Currents,' vol. i. chap. xxi.

and may be briefly stated as follows :—

Let P and Q be two impedances, then $\frac{P^2}{Q}$ will be an impedance, and may be termed the reciprocal of Q with respect to P.

Consider any network of the ladder type as fig. 7 having an impedance X, thus

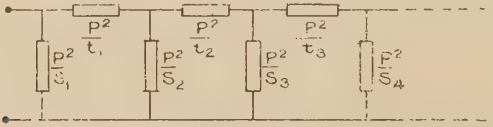
Fig. 7.



and consisting of a number of series elements S_1, S_2, S_3, etc. and shunt elements t_1, t_2, t_3, etc.

Construct a network having shunt elements $\frac{P^2}{S_1}$, $\frac{P^2}{S_2}$, $\frac{P^2}{S_3}$, and series elements $\frac{P^2}{t_1}$, $\frac{P^2}{t_2}$, $\frac{P^2}{t_3}$, as in fig. 8 :

Fig. 8.



and let its impedance be Y. Then it can easily be shown that

$$Y = \frac{P^2}{X},$$

i. e. Y is the reciprocal of X with respect to P.

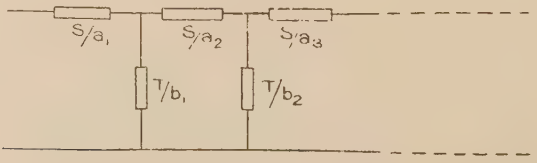
Returning to the case of $Z_0 \coth n\theta$.

$$Z_0 \coth n\theta = Z_0^2 / Z_0 \tanh n\theta,$$

and is thus the reciprocal of $Z_0 \tanh n\theta$ with respect to Z_0.

Therefore we can write down a network for $Z_0 \coth n\theta$ by reciprocating the network of fig. 4 with respect to Z_0, obtaining the result of fig. 9 :

Fig. 9.



where S, T, a_1, a_2, etc. and b_1, b_2, etc. have the same meaning

as in fig. 4. From these networks others can be derived by replacing θ by $\left(\theta + j\frac{\pi}{2}\right)$; this substitution changes $\coth\theta$ to $\tanh\theta$, and vice versa; if n is even, $\coth n\theta$ and $\tanh n\theta$ remain unchanged; if n is odd, $\coth n\theta$ is changed to $\tanh n\theta$, and vice versa. Thus in the networks of figs. 4 and 9, if n is even the interchange of $\tanh\theta$ and $\coth\theta$ throughout the network does not change its value, whereas if n is odd, the interchange changes the impedance of the network from $Z_0 \tanh n\theta$ to $Z_0 \coth n\theta$, and vice versa.

Taking the identity,

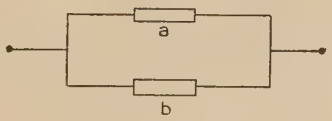
$$Z_0 \tanh n\theta$$

$$= \sum \frac{Z_0 \tanh\theta \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{2r+1}{2n}.\pi}}$$

$$= \sum \frac{1}{\dfrac{1}{Z_0 \tanh\theta . \dfrac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}} + \dfrac{1}{Z_0 \coth\theta . \dfrac{2}{n \cos^2 \dfrac{2r+1}{2n}.\pi}}}.$$

Now the expression under the Σ is the impedance of the network of fig. 10:

Fig. 10.



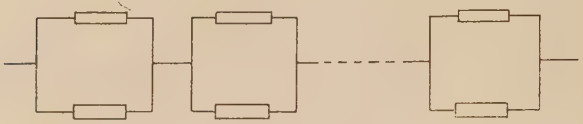
where

$$a = Z_0 \coth\theta . \frac{2}{n \cos^2 \dfrac{2r+1}{2n}.\pi},$$

$$b = Z_0 \tanh\theta . \frac{2}{n \sin^2 \dfrac{2r+1}{2n}.\pi}.$$

Thus $Z_0 \tanh n\theta$ is the impedance of the network fig. 11:

Fig. 11.



consisting of $\frac{n}{2}$ elements as fig. 10 connected in series.

Reciprocating with respect to Z_0, we have $Z_0 \coth n\theta$ as the impedance of the network of fig. 12:

Fig. 12.

consisting of $\frac{n}{2}$ shunt elements,

where $$c_r = Z_0 \tanh\theta \,.\, \frac{n}{2} \cos^2 \frac{2r+1}{2n} \,.\, \pi$$

and $$d_r = Z_0 \coth\theta \,.\, \frac{n}{2} \,.\, \sin^2 \frac{2r+1}{2n} \,.\, \pi.$$

Taking the expansion,

$$Z_0 \coth n\theta = \frac{Z_0}{n}(\tanh\theta + \coth\theta) + \sum_{r=1}^{r=\frac{n}{2}-1} \frac{Z_0 \tanh\theta \,.\, \dfrac{2}{n \sin^2 \dfrac{r\pi}{n}}}{1 + \dfrac{\tanh^2\theta}{\tan^2 \dfrac{r\pi}{n}}},$$

in the same way $Z_0 \coth n\theta$ is the impedance of a network of the form of fig. 11.

Reciprocating with respect to Z_0:

$Z_0 \tanh n\theta$ is the impedance of a network of the form fig. 12.

Results of similar form follow when n is odd.

Thus it will be seen that both $Z_0 \tanh n\theta$ and $Z_0 \coth n\theta$ can be represented by alternative networks either of the

form of a ladder network or a number of simple impedances connected either in series or in parallel.

It will be seen that these results are analogues of results previously given for the uniform line*. Both in the case of the artificial and of the uniform line the equivalent networks for $Z_0 \tanh n\theta$, $Z_0 \coth n\theta$, $Z_0 \tanh \mathrm{Pl}$, and $Z_0 \coth \mathrm{Pl}$ that take the form of a number of simple networks connected in parallel may be regarded as statements in physical form of the corresponding Heaviside expansion for the input current.

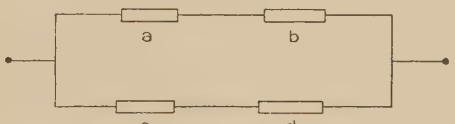
From these results many other networks for $Z_0 \tanh n\theta$ and $Z_0 \coth n\theta$ can be derived.

$Z_0 \tanh \frac{\theta}{2}$ and $Z_0 \coth \frac{\theta}{2}$ are physically realizable, hence we can expand in terms of $\frac{\theta}{2}$; if n has a factor n_1, we can expand $\tanh n\theta$ in terms of $n_1\theta$, and we can also write

$$Z_0 \tanh n\theta$$
$$= Z_0 \tanh \{(n-r)\theta + r\theta\}$$
$$= 1 \Big/ \left\{ \frac{1}{Z_0 \coth (n-r)\theta + Z_0 \tanh r\theta} + \frac{1}{Z_0 \tanh (n-r)\theta + Z_0 \coth r\theta} \right\},$$

which is the impedance of the network fig. 13:

Fig. 13.



where
$$a = Z_0 \coth (n-r)\theta,$$
$$b = Z_0 \tanh r\theta,$$
$$c = Z_0 \coth r\theta,$$
$$d = Z_0 \tanh (n-r)\theta,$$

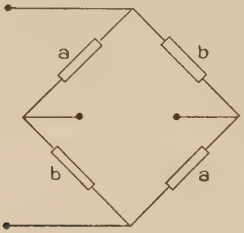
and expand the elements of this network.

The second result, namely the formation of a single Bridge type equivalent to any number of T, Π, or Bridge sections follows from a consideration of the relations between the propagation constant and characteristic impedance of the Bridge section and its impedance elements.

* Phil. Mag. Nov. 1924.

Consider a Bridge type section, fig. 14 :

Fig. 14.



where $$a = Z_0 \tanh \frac{n\theta}{2},$$

$$b = Z_0 \coth \frac{n\theta}{2},$$

its line characteristic impedance is Z_0 and its propagation constant is $n\theta$.

Thus, as regards both output and input terminals it will exactly replace an artificial line consisting of n sections such as fig. 3.

Now if n is even, $Z_0 \coth \frac{n\theta}{2}$ and $Z_0 \tanh \frac{n\theta}{2}$ are the impedances of $\frac{n}{2}$ Bridge sections of fig. 3 open or short circuited at the far end respectively; and if n is odd, the impedances are those of $\frac{n-1}{2}$ Bridge sections of fig. 3 closed through $Z_0 \tanh \frac{\theta}{2}$ or $Z_0 \coth \frac{\theta}{2}$ at the far end respectively. Further, from the previous sections we know that if $Z_0 \tanh \frac{\theta}{2}$ and $Z_0 \coth \frac{\theta}{2}$ are physically realizable, we can form other networks having impedances $Z_0 \coth \frac{n\theta}{2}$ and $Z_0 \tanh \frac{n\theta}{2}$.

Thus, given any Bridge type of artificial line consisting of any number of sections, we can construct a single Bridge type section that will replace it identically as regards both input and output terminals, and this can be done in a large number of ways.

Now returning to Π and T sections, in both cases $Z_0 \coth \frac{\theta}{2}$ and $Z_0 \tanh \frac{\theta}{2}$ are physically realizable, as also are $Z_0 \tanh \frac{n\theta}{2}$ and $Z_0 \coth \frac{n\theta}{2}$). Thus we can construct a single Bridge type section, and this in a large number of ways, equivalent to any number of given Π or T sections.

LXXVIII. *Ultimate Rational Units and Dimensional Theory.* *By* Prof. Gilbert N. Lewis, *Ph.D.**

THERE have appeared recently several criticisms of the theory of ultimate rational units which demand reply. When my recent paper appeared in the Philosophical Magazine †, one of the editors (O. J. L.) felt impelled to protest against the theory of ultimate rational units in a note appended to my article. However, since there is nothing in this note with which I cannot fully agree, one of us must misunderstand the other.

Next, Dr. Norman Campbell ‡ has, in a highly provocative paper, attacked the theory of ultimate rational units. He begins by saying: "'O. J. L.,' in appending to this last paper some general objections to Prof. Lewis's arguments (in which I concur entirely), has omitted to draw attention to the simple reasoning whereby it can be demonstrated to be false." This reasoning will be analyzed presently. Meanwhile it is to be noted that Dr. Campbell himself appears dissatisfied with his formal proof, and proceeds to a psychoanalytical investigation of my motives in propounding the theory, and of Planck's motives in not refuting it §, and he ends by stating that the theory of ultimate rational units may prove true, but, if so, that it will be useless, which seems incompatible with the statement that it is "demonstrably false." Nevertheless, when allowance is made for the vivid forensic style of Dr. Campbell, I find that I can agree with the greater part of what he writes (except always where he purports to state my own views), and, again, we must inquire what deep-seated misunderstanding on the one side or the other has provoked so heated a polemic.

* Communicated by the Author.

† Phil. Mag. xlv. p. 266 (1923).

‡ Phil. Mag. xlvii. p. 159 (1924).

§ Dr. Campbell gathers "from Planck's exposition of that subject that he judged the errors which have led Prof. Lewis astray too obvious to be worth noticing explicitly."

Finally, I shall refer to a criticism contained in the very stimulating little book of Bridgman on "Dimensional Analysis"*. Here he states, referring to one of the consequences of U.R.U., "It is undeniable that the result is of such simplicity that it seems probable that the coefficient may be the result of a mathematical process, and is not merely due to a chance combination of elements in a dimensionally correct form," but adds, "The justification of this point of view (theory of U.R.U.) at present is not to be found in any accurate results of measurement, but is rather quasi-mystical in its character." In the course of this article we shall find occasion to examine this question and attempt to ascertain just what is the quasi-mystical element that enters into the new theory.

In examining these various criticisms, it has seemed to me that the source of the feelings of opposition engendered by the statement of the theory of U.R.U. springs from certain prevailing ideas concerning the dimensions of physical quantities, and it seems therefore desirable to show once more, as Dr. Adams and I did in our original article †, that the theory of ultimate rational units may be presented without any statement or implication concerning dimensions.

The Simplest Statement of the Theory of Ultimate Rational Units.

Admitting that the centimetre, the gram, the second, and the degree are units which possess no profound theoretical significance, it is legitimate and desirable to inquire whether new sets of units may not be invented which will lead to a simplification of the equations of physics. Such an attempt was made by Planck, who employed for the fixing of his new units four experimental constants of universal importance—namely, the velocity of light c, the Boltzmann constant k (gas constant for one molecule), the Planck constant h, and the constant of gravitation f. His method consisted merely in finding units of mass, length, time, and temperature which would make each of these constants *numerically* equal to unity. The first two steps taken by Planck were also taken by Adams and myself, and I doubt if anyone familiar with the present state of physical science, and willing to attempt the reform of the system of units, would do otherwise than eliminate first of all the k which is

* Yale University Press, 1922.
† Phys. Rev. iii. p. 92 (1914).

affixed to temperature T in every fundamental equation of kinetic theory and of thermal radiation, and the c which accompanies the time t in all of the equations of electromagnetism and of relativity.

Our third step departs from Planck's procedure and makes use of the charge upon an electron *. Now, no one will question that this charge, which is that of a singly-charged ion, positive or negative, is a quantity of really fundamental significance. Nevertheless, if we decide to make this quantity the unit of electric charge, it still remains to define unit charge in terms of units of length, time, and mass before we can take the third step toward the reform of our present units. The dilemma may be illustrated by considering the third step of Planck's procedure. In certain fields of quantum theory the constant h seems no more fundamental than the constant $h/2\pi$, but if Planck had decided to make the latter constant numerically equal to unity, he would have arrived at an entirely different set of units. A similar ambiguity arose in connexion with the third step of our procedure, since two systems of electrostatic units were already in vogue. If e represents the charge upon an electron in ordinary electrostatic units, the same charge in Heavyside electrostatic units becomes $(4\pi)^{\frac{1}{2}}e$. Which of these two numerical values should be placed equal to unity? In fact, we chose neither of these, but rather the value $4\pi e$. In other words, we chose $(4\pi e)^2$ to be our new unit of energy × length. We admitted that this decision, which seems arbitrary, was reached after looking ahead to some of its consequences. But even if the decision should appear to be purely arbitrary, it is a perfectly legitimate attempt to improve our existing set of units.

The fourth step corresponding to Planck's use of the constant of gravitation we have not yet taken, so that for the present we are content to employ any set of units which makes c, k, and $4\pi e$ numerically equal to unity. For example, we may preserve provisionally the centimetre as the unit of length, and thus determine the three new units of mass, time, and temperature. With such a set of units we stated, as our new theory, that if such a system of units be

* Dr. Campbell devotes much space to proving the somewhat elementary proposition that it is not always possible to define n units by means of n constants. Thus it would be impossible to define units of mass, length, and time by means of the three constants c, h, and e (electron charge). He does not claim, however, that we have used such a set of constants, and his remarks do not seem therefore pertinent to the present discussion.

employed, "then all universal constants will prove to be pure numbers, involving only integral numbers and π." Our first application of this theory was to the constant of Stefan's law, and we asserted that this constant (radiant energy per unit volume at unit temperature) is numerically equal to unity when energy, volume, and temperature are expressed in our new units. This assertion was in agreement with experimental determinations of Stefan's constant within the wide limits of experimental error which at that time existed.

The whole proof of the demonstrable falsity of the theory of ultimate rational units brought forward by Dr. Campbell is that, no matter how narrow the experimental limits of error may be, there always remains within these limits an infinite number of values consistent with the experiments. But this is not a disproof of the theory of ultimate rational units, but rather a statement that from a purely logical standpoint no proof of any physical theory can ever be obtained. If, however, we predict from our theory certain numerical values, and if with continual refinement of experimental technique the experimental results come nearer and nearer to the predicted value, this will come as near to a proof of the theory as most scientists demand.

We predicted that the constant σ of Stefan's law would be $5{\cdot}70 \times 10^{-5}$. From this, assuming Planck's radiation law to be either a true relation or a very close approximation to the truth, we predicted that the Planck constant h would prove to be $6{\cdot}560 \times 10^{-27}$. In the second volume of Planck's 'Wärmestrahlung,' which appeared at the same time as our paper, he gave $\sigma = 5{\cdot}54 \times 10^{-5}$ and $h = 6{\cdot}415 \times 10^{-27}$ as the best experimental values then obtainable. The present accepted experimental values are $\sigma = 5{\cdot}72 \times 10^{-5}$ and $h = 6{\cdot}554 \times 10^{-27}$. Hence I stated in my recent paper that "unless, therefore, we are to assume a bizarre coincidence, the recent determinations of the constants of Stefan and Planck furnish a striking justification of the ideas which Dr. Adams and I advanced." If further and better measurements of Stefan's constant lead to values nearer to the one predicted, we should be justified in considering the theory of ultimate rational units as proved for this one instance at least.

The second application of the theory of ultimate rational units concerned the universal constant which appears in the entropy equation of a monatomic gas. Here, also, I predicted that the expression for the entropy per molecule would prove to be numerically equal to unity after expressing

all the quantities involved in ultimate rational units *. This I have shown to be in remarkably good agreement with existing experimental data, and I predict that the agreement will become still better as the measurements are improved.

What is a Simple Number?

In my more recent formulation of the theory I have stated that any universal constant would, in terms of U.R.U., prove to be a simple number, and the question of how we may logically define a "simple number" has greatly troubled both Professor Bridgman and Dr. Campbell. Perhaps it would have been better if I had adhered to the more guarded statement given in our first paper which I have just quoted, but it seemed to me that such criticism would be to some extent disarmed by the fact that in the two cases where an unqualified prediction has been made, namely, for the constants of black-body radiation and of the entropy of the non-atomic gas, the number used was in each case unity, which would in general I presume be regarded as a simple number. In any case the simplicity of the number assigned to any universal constant would necessarily be relative to the physical conditions which are imposed. Thus, if in defining Stefan's constant we consider the energy radiated per second from a black watch-spring of given size and shape, we should again find the energy radiated to be proportional to the fourth power of the temperature, but the constant of proportionality would be a very complicated number owing to the shape of the spring. If, however, we eliminate such complications in so far as we can foresee them, we may expect our universal constants to be as simple numbers as those which appear, for example, in a short table of definite integrals. The concrete question which has been raised concerns the Planck radiation formula, which by direct integration gives (in U.R.U.) $ah^3 = \frac{8\pi^5}{15}$, where a is Stefan's constant and h is Planck's. If $a=1$ we obtain h as a rather complicated number. Is this consistent with our theory as stated? I cannot answer this question in any positive way, but from the fundamental character of the

* It seems that part of Dr. Campbell's objections to U.R.U. is due to his having made some simple mistake whereby he concludes that my value for the constant of the entropy equation is $N^{5\,2}$ instead of unity, where N is the Avogadro number. It is perhaps not surprising, therefore, that he considers the theory fantastic.

quantities involved, and from the lack of any obvious complicating "shape-factors" and the like, it is my belief that the constant h will prove to be a much simpler number than the one thus obtained, and therefore that Planck's radiation formula will prove to be only an extremely close approximation to the true radiation formula.

It is to be noted in this connexion that Bridgman, while criticizing the concept of a simple number, adopts and employs an idea of Einstein *, namely, that a suspected physical relation obtained by considerations of dimensionality becomes probable if the numerical coefficients involved are found to be small numbers. It might, however, be difficult to explain just what is to be meant by a small number.

Is there a Mystical Element in the Theory?

I think that every scientist at some time makes use of a vague principle which may be expressed as a belief in the simplicity of natural laws. This belief we may call mystical since we have not the slightest idea whether its undoubted usefulness is due to the structure of the objective world, or to some hitherto unanalyzed trait of human psychology. The theory of ultimate rational units was based consciously upon this belief, and therefore Bridgman is perhaps justified in calling it quasi-mystical. All that I desire to point out here is that every physicist employs the same principle in other but quite analogous ways.

When the change of the mass of an electron with its velocity was first being studied, there were two rival theories, one of Abraham and one of Lorentz. However, the equation obtained by Abraham was so complicated that it seemed unlikely that it could be an exact expression for so simple a phenomenon, although the first experiments seemed to favour it. No one now doubts the accuracy of the very simple equation which was advanced by Lorentz.

Since, however, this illustration may appeal only to a limited number, let us consider some far more familiar applications of the principle of simplicity. When Stefan proposed a purely empirical equation † for the emission of radiant energy from a black body, he introduced 4 as the exponent of temperature in that equation, which agreed with

* *Ann. Phys.* xxxv. p. 679 (1917).

† The exactness of this equation was later proved thermodynamically by Boltzmann. Many such examples of experimental equations which have later been theoretically deduced tend to confirm our belief in the principle of simplicity.

observations within the limits of experimental error ; but, as Dr. Campbell would say, "so also would infinitely many other values." Again, let us consider Newton's law of gravitation. Neither the observations which had been made in Newton's time nor the more accurate ones which have since been obtained would enable us to say that the exponent of the distance in the gravitation equation is exactly 2 and not some number which differs by a minute amount* from 2. If we find deviations from Newton's law our instinct is not to make a slight change in the exponent, but rather to invent some entirely new functional relationship which may reduce to the inverse square law in the limit.

The fact that all the equations of physics which are regarded as at all fundamental contain exponents which involve only integers or simple fractions, is a striking example of the universal belief in the essential simplicity of natural laws.

Instead of writing the laws of Stefan and of Newton in their complete form, let us write

$$\frac{E}{V}=aT^r\ ;\quad F=f\frac{m_1m_2}{r^q}.$$

The theory of ultimate rational units states that the same "mystical" principle which leads us to expect the exponents of such quantities as T, r, and m_1 to be simple numbers, leads also to the expectation that the coefficients a and f will appear as simple numbers, when such units as are based on the circumference of the earth and the density of water are eliminated.

The Dimensions of Physical Quantities.

All that is essential to the theory of ultimate rational units can be stated without any reference to the physical dimensions of the magnitudes considered. It is perhaps unfortunate therefore that in my recent exposition of this theory I superimposed upon it certain considerations which introduced so controversial a subject as the theory of dimensionality ; for while I consider that such considerations are valuable, they seem to be almost solely responsible for the opposition which my paper has aroused. There is a taint of heresy attached to any suggested modification of the

* It is true that some authors have proposed a different exponent of r in the gravitation equation : for example, 2·0000002. If such an equation were to be adopted it would be interesting to inquire into the dimensions of the constant of gravitation.

orthodox statements regarding fundamental and derived magnitudes. Dr. Campbell challenges me to an admission of heresy by propounding the following dilemma :—"Either the statement that such a derived magnitude (*e. g.* velocity) has the conventional dimensions (*e. g.* lt^{-1}) is the expression of some scientific law or fact; or it is not." ..... "If it is not such an expression, but is a mere convention, then it is impossible to deduce from it anything scientifically significant, whether true or not." I have no fault to find with this statement, although he has chosen a magnitude which has never so far been defined otherwise than dl/dt. But referring to derived units in general, I do emphatically assert that the dimensions which they are assigned are the result of mere conventions (although these conventions are extremely useful), and it is impossible to deduce anything scientifically significant from the assumption that these dimensions are inherent in the nature of the measured magnitudes.

It would be difficult to overestimate the importance of the introduction of the system of fundamental and derived units which is due to the great genius of Gauss. Nevertheless, any particular system of this character is essentially conventional. There is nothing in natural laws which prescribes the choice of any particular measured magnitude, or of any particular number of such magnitudes which may be taken as fundamental. Furthermore, after the establishment of a definite set of fundamental units the derived units are not uniquely determined, nor are their dimensions. It is customary to choose some important relation between the derived magnitudes and the fundamental magnitudes, in order to determine the unit of the derived magnitude and also (through a distinct step which is by no means necessarily consequent upon the first) its dimensions. Thus angle is a typical measured magnitude. It may be expressed in various units. Solid angle may be considered to have the square of the dimensions of plane angle in precisely the same sense that an area can be considered to have the dimensions of the square of a length. Nevertheless, we decide to regard angle as a derived quantity. Having noted the relation that an angle is proportional to the length of an arc divided by the length of a radius, or

$$\text{angle} = \text{const.} \times \text{arc} \div \text{radius},$$

we choose the unit of angle such that the constant is unity. Changing the value of this constant, however, to unity does not affect its dimensions, and it is only by a completely

separate step that we make this constant dimensionless by definition, and thus make angle itself dimensionless. Sometimes we find more relations of importance between derived and fundamental quantities than are necessary for the definition of the derived units and dimensions. If we make equal use of all these relations, and are not especially lucky, we shall find that we have conflicting definitions of some of our derived quantities, either with respect to units or to dimensions or to both. But the conflicts may often be removed, either by abandoning one or more of the defining relationships or by changing the set of fundamental units.

The classical example of such a conflict is found in the electric and magnetic units. Gauss proposed that unit electric charge be defined by making the constant equal to unity in Coulomb's law for the force between two charged bodies. It was generally assumed later that this implied fixing the dimensions of charge by making this unit constant dimensionless. Similarly, Gauss proposed to define unit magnetic pole, and this also was assumed to carry with it corresponding implications regarding dimensions. All this would be perfectly satisfactory had it not been for the fact that the principle of Ampère furnished an independent and equally simple method of defining magnetic quantities in terms of purely electric quantities and the fundamental magnitudes, thus leading to another set of units, and presumably also of dimensions, for magnetic quantities.

Thus was created a dilemma which led to a great deal of discussion nearly half a century ago. In the year 1882 in the Philosophical Magazine alone there appeared a dozen papers on dimensions and units by Sundell, Helmholtz, Clausius, and many of the leading physicists of England. Among the latter was Dr. Oliver J. Lodge, who pointed out the striking difference between the points of view of the continental and the English authors. This difference may best be expressed by the statement that the continental authors laid greater stress upon the *units*, while the English authors laid more stress upon the *dimensions* of physical quantities. Thus Helmholtz had no objection to reducing mass to the role of a derived quantity (as indeed had first been suggested by Gauss himself), both with respect to units and dimensions, by employing the law of gravitation as the defining relation, and making the constant of that law numerically equal to unity and also dimensionless, so that he wrote

$$\left[\frac{M}{L^2}\right] = \left[\frac{L}{T^2}\right].$$

This same line of thought was developed extensively in the very able paper of Sundell. Bridgman states that "Planck was the first to think of the possibility of absolute units." He will find in this paper by Sundell, written in 1882, a very full discussion of many sets of absolute units in which he employs successively various numbers of fundamental units, and determines derived units by making the proper number of fundamental constants each equal to unity. At the same time he makes them dimensionless. For example: "If, in doing this, we wish to make the unit of time a derived unit, we must put

$$1 \text{ sec.} = 31 \times 10^{10} \text{ millimetres.}$$

Time must therefore be expressed as a length." He then shows that by using one set of constants, he obtains "a system in which the unit length is the only fundamental unit. The three electrical units now combine into one."

This last is also true of the dimensional system which I based upon the theory of ultimate rational units (although it is independent of and not necessary for the statement of that theory). In the system that I outlined, not only do the various units and dimensions of electric and magnetic quantities become identical, but the dimensions of all electric and magnetic quantities become integral, thus doing away with the fractional dimensions which are now ascribed to the majority of these quantities, and which many have felt to be a blemish upon the existing system of dimensions.

The paper of Sundell did not receive the attention which was its due, and the whole theory of dimensions, especially of electric and magnetic quantities, fell into confusion which was only apparently alleviated by a well-known paper of Rücker *, in which he showed that the various systems could be made mutually consistent by assuming that certain dimensions might be regarded as having been "suppressed"—namely, those of di-electric constant and of magnetic permeability. Unfortunately, however, he gave no rule for deciding under what circumstances it was necessary to restore the dimensions which have invariably been suppressed in the definition of every derived quantity. Thus we might decide to restore dimensions that have been suppressed, as we have just seen, in the definition of angle.

Something like this was actually suggested by Williams †, who proposed to introduce three fundamental dimensions

* Phil. Mag. xxvii. p. 104 (1889).
† Phil. Mag. xxxiv. p. 234 (1892).

corresponding to length, namely [X], [Y], [Z], so that the dimensions of area would be represented by [XY] and of angle by $[XY^{-1}]$. But even in this method of representing angle, the dimensions, if such there be, inherent in the constant of the relation—angle proportional to arc divided by radius—are still suppressed. Of course, the answer to all such questions is that no quantity whatever has any intrinsic or absolute dimensions, but only the dimensions which we agree to ascribe to it.

One of the reasons for the proposals of Williams was that he objected to having two different types of magnitudes represented by the same unit. The same thought appears to have been in the mind of "O. J. L." when he appended his note to my previous paper, and said that "Length and Mass and Time and Energy and Momentum are not the same. Nor is Temperature identical with Energy. Different things sometimes appear to be of the same dimensions, like Work and Moment of force; but there is an element of direction involved even there, and a scalar product differs from a vector product." Such an element of direction is not always present. If we consider the fraction of a mass of radium which disintegrates per second, we are dealing with a quantity of the same dimensions as the rate of change of a solid angle with the time, and both quantities are scalar. However, no one would think of regarding them as identical. Even using more than three fundamental magnitudes, such coincidences would occasionally occur, and their number will obviously increase as we diminish the chosen number of fundamental magnitudes. Nevertheless, in some cases these coincidences will suggest the existence of hitherto unsuspected identities. For example, those who are familiar with the four-dimensional representation of relativity recognize mass and momentum as two projections of the same vector of extended momentum *, and the fact that the new system of dimensions that I have proposed gives energy the same dimensions as frequency is very suggestive in the light of present views on spectroscopy.

On the other hand, some have objected to the reduction of the number of fundamental magnitudes on the ground that this would restrict the scope and usefulness of the methods of dimensional analysis. This, however, is not the case. All the valid results which are obtainable by these methods can be obtained equally well in a system of any number of fundamental magnitudes. Thus Rayleigh obtained a solution for a certain problem in the interchange of

* See Wilson & Lewis, Proc. Amer. Acad. xlviii. p. 389 (1912).

heat, using heat and temperature as two additional fundamental magnitudes; but Riabouchinsky *, employing the mechanical theory of heat and thus adhering to the ordinary simple set of fundamental magnitudes, was unable to obtain the same solution. In his reply Rayleigh said: "It would indeed be a paradox if the further knowledge of the nature of heat afforded us by molecular theory put us in a worse position than before in dealing with a particular problem." So we may also say that the recognition of the velocity of light as a quantity fundamental to all kinematics cannot in any way diminish the content of our previous knowledge.

The whole method of dimensional analysis contains so much that is sound and so much that is unsound that a full logical analysis of the problem has long been needed. Fortunately such a complete analysis in extremely satisfactory form is furnished by a recent paper of Mrs. Ehrenfest †. It seems to me that her conclusions are indisputable, and that they clarify to an extraordinary degree the whole problem of the methods of "model" equations and dimensional equations. One of these conclusions is that "The very widespread method of determining, on the basis of the demands of homogeneity, the form of equations as yet unknown, between magnitudes whose dimensions are already fixed, has no foundation and in general may lead to errors"

In other words, if we have a problem of determining the functional relationship between physical variables in a system of which the behaviour is determined by known differential equations, but of such complexity that integration of these equations is inconvenient or impossible, the problem may be solved in identical manner either by the method of dimensional equations or by the method of "model" equations. Both methods lead to identical results, although in using the method of models not a word need be said regarding the dimensions of physical quantities.

On the other hand, for the prediction of an unknown relation between physical quantities, the common method of dimensional analysis has no logical or mathematical basis. If we continue to employ it in the hope that it may lead to useful results, this hope must be based not upon any established principles of science, but upon some vague belief in the simplicity of nature.

* Quoted in Bridgman's 'Dimensional Analysis.'

† T. Ehrenfest Afanassjewa, *Math. Ann.* lxxvii. pp. 259–276 (1916).

LXXIX. *Units and Dimensions.*

I WOULD ask Professor Lewis (p. 739) whether he is not attaching undue importance to the numerical part of physical quantities, and trying to regard actual things as if they were or might be pure numbers.

By choosing units we can easily control the numerical part of a specification, and make it 1 if we like; we cannot control the thing itself. The specific gravity of water at 4° is not 1; it is 1 gramme per c. c. The velocity of light is not 1, nor yet 3×10^{10}; it is not a number at all, but a concrete reality.

Arithmetic and counting do not naturally apply to continuous quantities: hence the device of artificial units. Recent Atomism and Discontinuity have given to the operation of counting greater prominence, or at least larger scope, than formerly; for now, surprisingly often, we encounter what seem to be natural units that ask to be counted. But still we must specify what we are counting; otherwise, one might count the oranges, another the bushes, and another the pips.

Every physical quantity has a nature of its own, and it is the reverse of helpful to mask or disregard it. We do not know what an electric charge is, but we know that it is something real and not an abstraction; no mere number can express it. The equation $F = = ee'/K_0r^2$ represents not a convention but a fact of nature. To take K_0 as 1 is a confession that we do not know its real nature and nevertheless wish to employ a practical system of electrical measurement to tide over the time of our ignorance. It would have been equally legitimate, and in some ways more convenient, to take it as 4π; but considerations of that kind are of small importance.

If we prefer to express a charge by counting the electrons on a charged body, then K_0 would be something like $\frac{1}{2}10^{19}$ c.g.s. units. But until we know more, we cannot really measure e or K_0. Nor can we express any Ether quantity dynamically, unless two unknowns cancel out. What we measure is not e but $e/\sqrt{K_0}$.

We may hereafter arrive at a more fundamental dynamics, appropriate to the Ether, and be able to express electric and magnetic quantities in terms of space, time, and some more fundamental conception than mass. Always the actual nature of quantites is the important thing; and about that our statements are by no means conventions, for they may be

true or false. If we say that RC is time, that RI^2 is power, that capacity is a length, and that e^2 or $(4\pi e)^2$ is energy $\times$ length, we are making fundamental statements; and of these the first two are true, while the last two are false.

I seem to be saying elementary things, and perhaps Professor Lewis agrees with me. If so, I am out of the controversy, which then turns on what units are the most convenient, with our present limited knowledge, for practical purposes.

OLIVER J. LODGE.

LXXX. *Semi-optical Lines in the X-ray Spectra.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper published in the February number of the Phil. Mag. by Messrs. Bäcklin, M. Siegbahn, and R. Thoræus on "Semi-optical Lines in the X-ray Spectra" (Phil. Mag. vol. xlix. p. 513, Feb. 1925) we have seen that many conclusions on the apparition of X-ray lines in the periodic system and on the electronic structure of the elements are said to be new ones, although they have been pointed out by us more than a year ago (*Journal de Physique et le Radium*, t. v. pp. 1–19, Janvier 1924)*. In the discussion of Mr. Hjalmar's results on the starting up of $K\beta$ and $K\gamma$ lines in the K series of light elements (Phil. Mag. vol. xli. p. 675, April 1921, and *Zeitschrift f. Physik*, vii. p. 341, 1921) we have clearly shown that Mr. Hjalmar's lines cannot be explained in another way, and that, in accordance with our system of atomic structure but in opposition with that of Prof. Bohr, the $K\beta_1$ line just starts up for aluminium and $K\gamma$ for scandium. These statements are well illustrated by the accompanying table and diagram, which are taken from our above-quoted paper; the table was published by us for the first time as soon as 1922 (*Comptes Rendus de l'Académie des Sciences*, t. 175, p. 755, Oct. 1922).

Let us finally note that Messrs. Bäcklin, Siegbahn, and Thoræus ascribe to Stoner (Phil. Mag. p. 286, Oct. 1924) the first idea of the following repartition of the electrons amongst the L levels:

$$2L_3, \quad 2L_2, \quad 4L_1,$$

although this was previously experimentally checked by one

* In this paper we have denied the relativistic nature of the so-called "regular L doublets," a conclusion which was also later on reached by many authors (Landé, Millikan, and Sommerfeld himself).

[To face page 752.

Series of Rontgen Rays.

Optical series.

N Bohr et A Sommerfeld

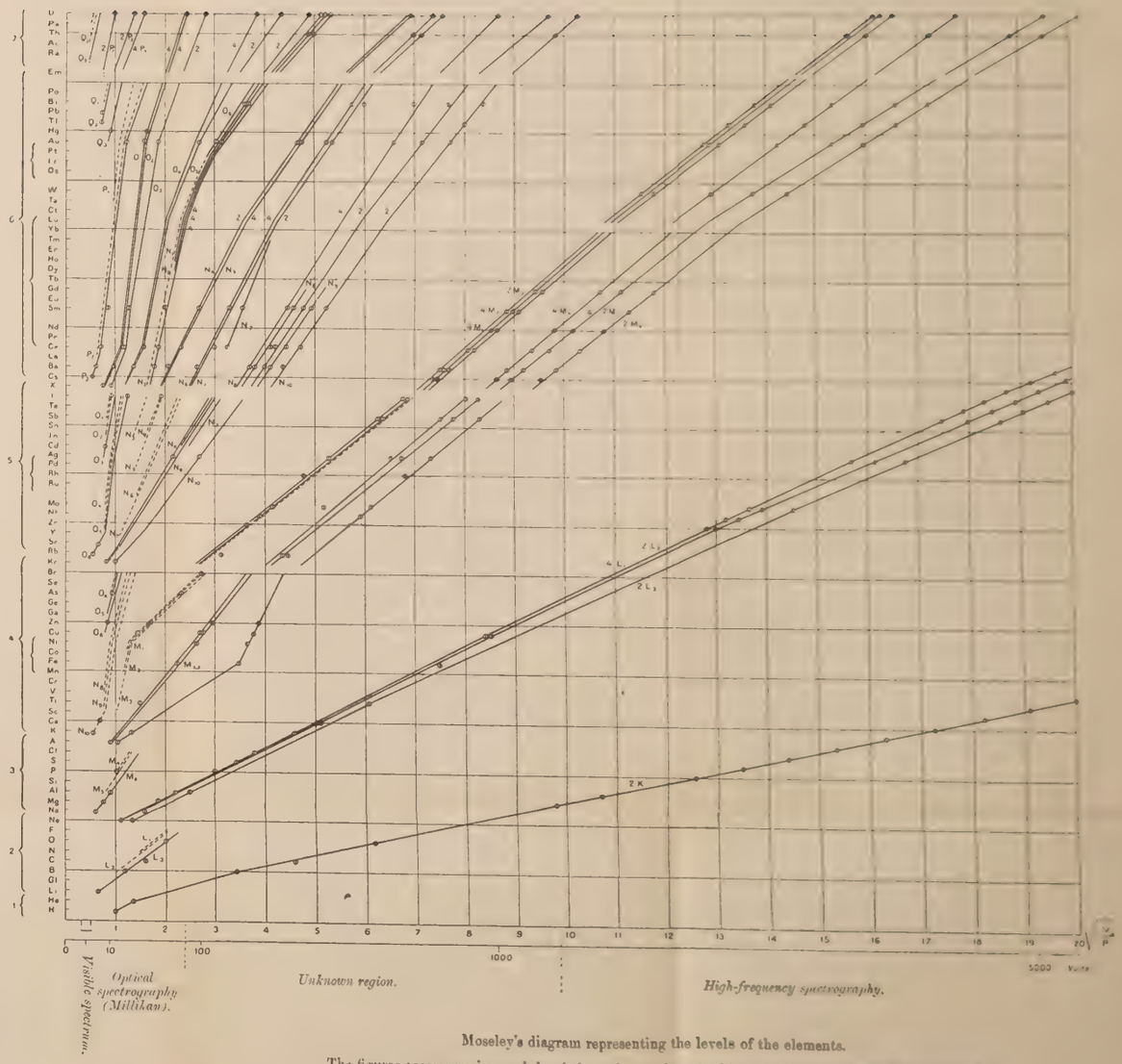
Regular doublets. Degenerate level. Irregular doublets. Equatorial quants. Radial quants. Latitude quants. Azimuthal quants.

Number of orbits. Arrival levels.

Serie K	Séries L			Séries M						Séries N										Séries O						Séries P			Q
2	2	2	4	2	2	4	2	4	4	2	2	4	2	4	4	2	4	4	4	2	2	4	2	4	4	2	2	4	
K	L_3	L_2	L_1	M_6	M_5	M_4	M_3	M_2	M_1	N_{10}	N_9	N_8	N_7	N_6	N_5	N_4	N_3	N_2	N_1	O_6	O_5	O_4	O_3	O_2	O_1	P_3	P_2	P_1	Q
100	110	101	200	120	111	210	102	201	300	130	121	220	112	211	310	103	202	301	400	120	111	210	102	201	300	110	101	200	100
1 (*s*)	1 (*s*)	2 (*p*)		1 (*s*)	2 (*p*)		3 (*d*)			1 (*s*)	2 (*p*)		3 (*d*)			4 (*f*)				1 (*s*)	2 (*p*)		3 (*d*)			1 (*s*)	2 (*p*)		1 (*s*)

	L_3 110	1 (*s*)																												
	L_2 101	2 (*p*)	α_2																											
	L_1 200		α_1																											
M_5	M_6 120	1 (*s*)			η	I																								
M_4	M_5 111		β_2	β_4		$\underline{t}$																								
M_3	M_4 210	2 (*p*)	β_1	β_3	β_{11}	$\underline{s}$																								
M_2	M_3 102			$\underline{\beta_9}$	β_1	α_2																								
M_1	M_2 201	3 (*d*)		$\underline{\beta_8}$	(β_{13})	α_1																								
	M_1 300					α_3																								
N_7	N_{10} 130	1 (*s*)			γ_5	β_6		r	r																					
N_6	N_9 121	2 (*p*)	*	γ_7			r			*	*										r									
N_5	N_8 220		γ_1	γ_3	»	»	r			*	*	r																		
N_4	N_7 112			»	γ_1	β'_2		ē	r																					
N_3	N_6 211	3 (*d*)		γ_9	*	β_2		*	Y																					
	N_5 310					β'''_2			*																					
	N_4 103				γ_{10}	β''_2				*	*																				
N_2	N_3 202	4 (*f*)			γ_6	β'_2				β	*	α_2																		
N_1	N_2 301									β''	*	α_1																		
	N_1 400									β'	*	α''																		
O_5	O_6 120	1 (*s*)			γ_{11}	β_7		*	r					r	*															
O_4	O_5 111	2 (*p*)	*	γ'_4			*			r	*			r		*	*													
O_3	O_4 210		δ_1	γ_4	»	»	r			*	*	?		r		*	*	*												
O_2	O_3 102	3 (*d*)		»	γ_2	*		r	*						r	*			*	*										
O_1	O_2 201			γ_{12}	*	β_5		*	δ						*	r			*	*										
	O_1 300					*			*							*			*	*										
	P_3 110	1 (*s*)			γ'_2	β'_5		*	*					*	?						*	*								
	P_2 101	2 (*p*)	*	*			r			*	*	r		*		*	*				*			*	*					
	P_1 200		*	γ_8			*			*	*	r		r		*	*	*			*			*	*					
	Q 100	1 (*s*)			*	*		*	*						*	*						*	*					*	*	

Optical series



Moseley's diagram representing the levels of the elements.

The figures accompanying each level show the number of orbits of which it is definitely constituted.

of us (A. Dauvillier, *Comptes Rendus*, t. 179, p. 476, Janvier 1924).

We hope that you will have the kindness to publish in your Journal this priority claim and also, if it is possible without trouble, the accompanying table and diagram.

Yours sincerely,

Louis de Broglie,
A. Dauvillier.

Laboratoire de Recherches Physiques
sur les Rayons X, Paris, 12 rue Lord-Byron,
Feb. 17, 1925.

LXXXI. *On the Electrical Conductivity of Metallic Solid Solutions.* *By* Eustace J. Cuy, *Ph.D.**

(Contribution from the Department of Chemistry, Yale University.)

IN a very recent article Höjendahl † has discussed "the electrical conductivity and certain other properties of metals and alloys on the basis of the Bohr theory."

In a letter to Professor P. W. Bridgman some time ago (December 16th, 1923) I had expressed some similar views arrived at independently and from different sources of evidence. It may not be out of place to summarize them briefly, since, although in some parts they coincide with those of Höjendahl, in others they complement them.

It is a well-known fact that the electrical conductivity of a metal decreases if a second metal is added to it capable of forming solid solutions with it. By solid solution, or mixed crystals ‡, is meant that from the liquid state both substances crystallize together, giving, as far as microscopic examination can detect, a perfectly homogeneous solid phase of variable composition, whose *physical properties vary continuously* from those of pure A to those of pure B. If the specific electrical conductivity is plotted against the composition in per cent. (weight, volume, or mole), a curve very similar to a catenary is obtained. This is not true, if the two pure metals or intermetallic compounds crystallize separately from solution giving a mechanical mixture known as a eutectic. In this case the conductivity-composition (λ–x) curve is made up of one or more straight lines depending upon the presence or absence of intermetallic compounds §.

* Communicated by the Author.

† Höjendahl, Phil. Mag. xlviii. p. 342 (1924).

‡ It should be very carefully noted that the very common term "mixed crystals" is a misnomer. It does not signify a mechanical mixture of different kinds of crystals, but a homogeneous crystal of variable composition (mixed with something else).

§ A very good treatment of this subject is to be found in Tammann's *Lehrbuch der Metallographie*, Voss, Leipzig, 1921, pp. 304–315.

Several attempts to account for the catenary form of the electrical conductivity-composition curve of solid solutions have been made, none of which can at present be considered as successful.

Lord Rayleigh * and Liebenow † have attempted to account for it by assuming that the apparently homogeneous solid solutions consisted of very small submicroscopic particles or plates of the pure components, which at their junctions developed counter-electromotive forces (Peltier effect). This, of course, would tend to decrease the electrical conductivity. Secondary and rather plausible assumptions enabled them to arrive at equations fitting very satisfactorily the experimental results. However, the recently-acquired knowledge as to the structure of crystals by means of X-ray analysis has made their fundamental assumption of submicroscopic inhomogeneity untenable.

Vegard ‡ has found that a KCl–KBr mixed crystal consists of a face-centred K lattice as in pure KCl or KBr and an interpenetrating also face-centred lattice of negative ions of the same lattice constant as the positive ion lattice, also exactly as in KCl or KBr, with the difference, firstly, that the negative ion lattice consists of Cl and Br ions arranged at random, and secondly, that the lattice constant of the mixed crystal is intermediate between that of KCl and KBr. The sharpness of the reflexion maxima, which was as sharp as that of the single salts, shows definitely the absence of groups of Cl or of Br ions arranged in such a way as to constitute even very small KCl or KBr particles microscopically indistinguishable.

Furthermore, Bain § has investigated the solid solutions of Au–Ag and Au–Cu by means of X-rays. In this case also the crystals were perfectly homogeneous. The lattice constant for Au is 4·08 Å., for Ag is 4·06 Å., and for the solid solutions of the two it has an intermediate value. For the alloys of Au–Cu (Cu is 3·60 Å.) the values were again between those of the components. However, there were small deviations from linearity in the direction of greater density (smaller lattice constant).

Another way of accounting for the low conductivity of solid solutions was based on the assumption that the mean

* Lord Rayleigh, 'The Electrician,' xxxvii. p. 277 (1896); 'Nature,' liv. p. 154 (1896).

† Liebenow, *Zeit. f. Elektrochem.* iv. pp. 201, 217 (1817); Nernst, Theoretical Chemistry,' Macmillan, London, 1911, 6th ed. p. 408.

‡ Vegard, *Zeit. f. Physik*, v. p. 17 (1921).

§ Bain, Chem. & Met. Eng. xxviii. p. 21 (1923).

free path of electrons in this case was considerably smaller than that in a pure metal, due to the presence at irregular positions of atoms of the second metal. The illustration commonly used was that in a pure metal the atoms were arranged as trees in a garden in definite rows, while a solid solution resembled a forest. A man (electron) could run through the garden much faster than through the forest. It is almost superfluous to state that the recent X-ray work quoted above makes the assumption of irregular arrangement of atoms in solid solutions entirely unjustifiable.

Rosenhain * has recently proposed an explanation for this phenomenon, best described by the following illustration. If a number of billiard balls of the same size are arranged in a row and the last one is struck, the total impulse will be transferred to the first one. If, however, among them there is one of larger radius, and the last one is again struck, then the large sphere will not transfer all its energy to the adjacent one, but there will be a lateral component which, in so far as direct propagation of energy is concerned, is lost. If such a view is correct, then using an atom of another element having the same radius (in the above illustration, a sphere of another colour but the same size) should not depress the conductivity. A particularly good example is the Au–Ag, system referred to above, whose crystal structure and parameters have been determined by Bain, and whose electrical conductivity has been studied by Matthiessen, Roberts, and Stroudhal and Barus†. The lattice constant of Au is 4·08 Å. of Ag 4·06 Å., and of mixed crystals the same (no shrinkage or expansion on mixing). Consequently the two kinds of atoms are equal in radius. It is therefore hardly to be expected that any decrease in conductivity should occur, since with equal atoms there is hardly any lateral component. And yet the conductivity composition curve is very nearly the same as in the other cases where the radii are unequal. In other words, the atomic radius does not play the role it should if the above explanation were correct.

Schenck ‡ has assumed that the second component does not decrease the mean free path, but decreases the concentration of the electrons. This, of course, would also lower the conductivity. In a sense this cannot be considered as a solution of the problem ; it merely changes the question : Why does the presence of B lower the conductivity of A ?

* Rosenhain, Journ. Inst. of Metals, xxx. p. 3 (1923).
† See Tammann's '*Metallographie*,' p. 309 (1921).
‡ R. Schenck, *Phyz. Zeit.* viii. p. 239 (1907).

to: Why does the presence of B lower the electron concentration of A ? *

It is evident that the classical theory of Drude or its various modifications cannot account for this depression of conductivity. J. J. Thomson† has suggested, in order to avoid the difficulty of the equipartition of energy of the electrons, that the electrons arrange themselves in quasi-rigid electron chains having the properties attributed by the classical theory to the individual electrons. It would be expected on this basis that the individual electrons or the electron chain should change their properties (concentration, velocity, mean free path, etc.) continuously upon the addition of a second component, giving a conductivity-composition curve approximately a straight line, but under no circumstances a catenary.

Also the possible explanation, based on the assumption that the amplitude of vibration of the atom passes through a maximum at 50 per cent. composition, making it more difficult for the electrons to travel through the alloy, must be rejected since, in addition to the lack of any theoretical foundation for it, it is empirically found that the conductivity depression is not, as a first approximation, a function of the atomic weight of the second component. This can be seen from the alloys of platinum ‡ with iridium, palladium, gold, rhodium, manganese, copper, and iron §. Similarly, the Cu–Ni and the Cu–Au systems give very similar λ-x curves, although their atomic weights differ by less than 8 per cent. in the former case, and one element is over three times as heavy in the latter.

Bridgman ‖ has suggested that "in metallic conduction the electrons pass through the substance of the atoms, and that the mechanism by which resistance is produced is intimately connected with the amplitude of atomic vibration. The number of free electrons is supposed to remain constant; their velocity is taken to be that of a gas particle of the same mass and temperature, and their mean free path to be many times the distance between atomic centres. . . . . *There is no necessity in supposing that a single free path is*

* Compare also Hauer, *Ann. d. Physik*, li. p. 189 (1916), who assumes an equilibrium between the free and the bound electrons.

† J. J. Thomson, Phil. Mag. xliv. p. 657 (1922).

‡ Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 5th ed., p. 1056 (1923).

§ It should be noted that the conductivity is plotted against the composition in *weight* per cent. The agreement would be very much better if mol. per cent. were used.

‖ Bridgman, Phys. Rev. xvii. p. 161 (1921).

straight; the electrons may perform Virginia reels about the nuclei of the atoms in quantum orbits *. Something of this sort probably has of necessity to take place in non-cubic crystals."

This, in conjunction with the following suggestion made to the author by Dr. Kurt Fischbeck, formerly of Göttingen, leads to the explanation for the low conductivity of metallic solid solutions. If instead of concentrations their reciprocals are used, then the conductivity of mixed crystals can be calculated on the basis of an equation of the form :

$$\lambda = \frac{\lambda_A}{X_A} + \frac{\lambda_B}{X_B} = \frac{\lambda_A}{X_A} + \frac{\lambda_B}{1 - X^A},$$

where λ, λ_A, and λ_B are the specific conductivities of the solid solution, of A and of B respectively, X_A and X_B the concentrations of A and of B respectively expressed in mol. per cent.† It is evident that the values of λ pass through a minimum at

$$X_A = X_B = 50 \text{ per cent.}$$

It is seen that it is not the concentration that is the important factor, but the groups or clusters of atoms of the same kind through which the electron can pass before coming across one of the opposite kind.

Benedicks ‡ has expressed the opinion that it looks as if atoms had definite channels through which electrons could travel, but which were of such a specific nature (their location, direction, etc., were different in different atomic species), that by mixing atoms of two good conductors the channels were more or less blocked, giving a poor conductor.

The following picture of the cause and mechanism of the conductivity depression due to mixed crystal formation at once suggests itself. At the absolute zero the atoms are at rest, and the electrons are still revolving in their quantum

* Page 171. The italics are mine.

† This equation would hold for very low temperatures. At more elevated temperatures it would assume the form :

$$\lambda = \frac{\lambda_A}{X_A - K_A} + \frac{\lambda_B}{X_B - K_B} = \frac{\lambda_A}{X_A - K_A} + \frac{\lambda_B}{(1 - X_A) - K_B},$$

where K_A and K_B are constants at a given temperature, and prevent the value of the conductivity of the pure metals ($X_A = 0$, $X_A = 1$) from becoming infinite. These constants are probably in some way related to the gaps present between groups of atoms, as will be discussed below.

‡ Benedicks, *Jahrbuch d. Radioakt. und Elektronik*, xiii. p. 351 (1916).

paths. The valence electrons, to which conduction is due, move in elliptical orbits having a definite frequency of rotation and of perturbation. It does not seem unlikely that these electrons keep in phase. When the electron is furthest from the atom to which it belongs, so are the electrons of all the other atoms. At that instant it is nearest to a neighboring atom. Therefore a potential difference would cause the electron when it is at its greatest distance from its atom, instead of returning to its own atom, to jump across to the not very distant quantum path of the neighbouring atom, thus accounting for the supra-conducting state.

This in a sense bridges over the Haber * theory of an independent electron lattice moving through the metal, the Thomson † theory of rigid electron chains moving in certain directions, and the Bridgman ‡ theory that resistance is caused by the difficulty of an electron jumping from atom to atom.

In a solid solution at the absolute zero the atoms are again at rest and the electrons revolving, but they are not now in phase, since the frequencies of rotation and of perturbation for the electrons of each atomic species are different. This accounts for the fact that supra-conductivity is not observed in solid solutions. In other words, the "gap trouble" does not exist since all the atoms are at rest, but the "phase trouble" does since two different kinds of atoms are mixed together.

Professor Bridgman has called my attention to the fact that recently some alloys of Sn and Pb and also some amalgams have been found to assume supra-conductivity. The Pb–Sn system does not give complete solid solutions (the metals are not miscible in all proportions in the solid state), but Pb contains 4 per cent. of Sn, and Sn only 1 per cent. of Pb. From the phase-rule diagram it appears that the solubility of the two metals in each other decreases on cooling. It is therefore possible that either or both metals may throw off all the foreign constituent at very low temperatures. In any case, however, the foreign atoms are very few. The amalgams, on the other hand, usually give eutectics (mechanical mixtures) of the pure metals as in the case of Hg–Zn, or of intermetallic compounds as in the case of Hg–Li or Hg–Na. As Professor Johnston has remarked, it is not necessary that all the metallic mass become supra-

* Haber, *Sitzb. preuss. Akad.* pp. 506, 990 (1919).
† J. J. Thomson, Phil. Mag. xliv. p. 657 (1922).
‡ Bridgman, Phys. Rev. xvii. p. 161 (1921).

conducting, since a few coherent threads of one supra-conducting metal are sufficient to cause the classification of the alloy as supra-conducting. It is, however, extremely probable that systems like Au–Cu, Ag–Au, etc., which give complete solid solutions, will never be found to exhibit supra-conductivity.

As the temperature is raised, the atoms will begin to vibrate and bigger and bigger moving gaps will appear, making it more difficult for electrons to jump from atom to atom—that is, causing an increase in resistance according to Bridgman's view.

In a metallic solid solution this gap source of resistance will be present to the same extent as in the pure metals at the same temperature. In addition, there will be the difficulty due to the electrons of unlike atoms not being in phase. Therefore a configuration which would have allowed an electron to jump to the next atom in a pure metal will not do so in an alloy—that is, the resistance will be greater. This is known to be the case.

Raising the temperature a given number of degrees will cause a given increase in resistance for reasons explained above. In a solid solution, however, this increase in the number and magnitude of the gaps will not have as great an effect as it did in the case of a pure metal, where it was the only source of resistance. To illustrate : in a pure metal, out of 100 possible electron jumps, 30 say are hindered by the accident that the atoms are far apart at that instant ; in a solid solution, out of 100 possible jumps, 50 say do not occur, due to the fact that the electrons of adjacent foreign atoms are not in phase, and 30 per cent. of the other 50 due to the gaps. Therefore the temperature coefficient of the resistance of solid solutions will be less than that of pure metals (15 per cent. as against 30 per cent. in the example given). This is in agreement with the experimental observations.

Bridgman has found that, in general, pressure renders metals better conducting. This, of course, is to be attributed to the fact that the gaps are made smaller by pressure. By analogous reasoning to that given above about the effect of temperature, it can be shown that the pressure-coefficients of solid solutions should be less than that of their components. This is also in agreement with experimental observations, since cases are known where the coefficients of alloys are not only smaller but even negative.

The well-known fact that the physical and chemical properties of components of an alloy (such as atomic weight,

valence, molecular volume, lattice constant, etc.) do not, as a first approximation, show themselves in the conductivity-composition curve is, of course, to be ascribed to the fact that the electron orbits are not a simple function of any of these variables. The great similarity of all λ-x curves is to be attributed to the fact that they all represent probabilities of favourable conditions making an interatomic jump possible.

The fact that, although the addition of a second metal to form a solid solution lowers the electrical conductivity very greatly, the addition of a third or fourth has relatively small effect* can be attributed to the small number of groups of atoms of A or of B which the addition of C or D can break up, since the presence of B has already made impossible the existence of any large number of atoms of A grouped together. Therefore our view that the increase in resistance due to the formation of solid solutions can be attributed to the absence of large groups of atoms of either kind, accounts for the smaller and smaller effect that additional components have upon the conductivity of an alloy.

It is not at present clear how the Franz-Wiedemann ratio could be derived for alloys from the views here given.

The phenomena described above will have to be explained by any generally valid theory of metallic conduction. They have up to the present been, to a large extent, neglected by physicists.

Summary.

A brief review of the theories of electrical conductivity has been given with particular emphasis on their application to metallic solid solutions. It is found that none of the accepted theories will account for the observed phenomena.

If it is assumed that the electrons responsible for metallic conduction move in quantum orbits, and in a pure metal are in phase with those of the adjacent atoms, then the following facts can be accounted for:—(1) The low conductivity of alloys consisting of one kind of crystals of variable composition; (2) their low temperature coefficient; (3) their low pressure coefficient; (4) the absence of the supra-conductive state; (5) the great similarity of the conductivity-composition curves of various mixtures, and (6) the absence of any specific effects due to the physical and chemical properties of the second metal added.

August 28, 1924.

* Fischbeck, *Zeit. f. anorg. Chem.* cxxv. p. 1 (1923).

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]